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The Heat of Dissociation of the Carbon-Carbon Linkage

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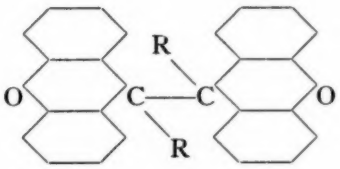
Ziegler's colorimetric measurements of the dissociation of hexaphenylethane provide information in regard to ΔF and ΔH for this process in solution. Assuming that ΔS for the dissociation of other similar compounds is approximately the same and independent of the temperature (over a short range), ΔF and ΔH of dissociation of a variety of compounds have been calculated from published data. It is suggested that the effects of substitution are approximately additive. There is evidence to indicate that the heat of activation of the association reaction of free radicals is very low; if this is the case the heats of dissociation estimated from the calculations of this paper provide information in regard to the heat of activation of the dissociation reaction.

THE heat of dissociation of the carbon-carbon linkage in simple aliphatic compounds such as ethane can be estimated from heats of combustion and an estimation of the heat of sublimation of carbon. The most probable value seems to be between 70 and 80 kg cal. If the six hydrogen atoms of ethane are substituted by six aryl groups such as the phenyl group, the resulting compound, hexaphenylethane, spontaneously dissociates in solution into the free radical triphenylmethyl. This and related phenomena have been extensively studied since the first discovery of triphenylmethyl by Gomberg more than thirty years ago. It is the purpose of this paper to summarize what quantitative data are available in regard to the dissociation of substituted ethanes and the free radicals containing trivalent carbon. We have been particularly interested in this laboratory[1] in the effect of alkyl groups (C_nH_{2n+1}) on the degree of dissociation of substituted ethanes, and have studied some years ago a variety of substituted dixanthyls all of which have the general formula



in which R may be either a hydrogen atom, an alkyl group, or an aryl group.

The most satisfactory work on the quantitative study of the dissociation of a compound into free radicals is that of Ziegler[2] who studied by a colorimetric method the degree of dissociation of hexaphenyl ethane in a variety of solvents. He also studied the dissociation at two different temperatures and thereby calculated the heat of dissociation. I shall use his measurements as a starting point for my calculations. Equilibrium constants at 293°K obtained by Ziegler for the dissociation of hexaphenylethane varied from 1.2 to 19.2 depending on the nature of the solvent. Expressing his results in terms of mole fractions,

[1] J. Am. Chem. Soc. **47**, 3068 (1925); **48**, 1743 (1926); **49**, 2080 (1927); **51**, 1925 (1929).

[2] Ziegler, Ann. **373**, 163 (1929).

the free energy of dissociation ΔF°_{293} varies from 6.8 kg cal. to 5.3 kg cal., the values of ΔH°_{293} from his own measurements vary from 10.5 kg cal. to 12.0 kg cal. Taking the mean of each of these results we may estimate that $T\Delta S$ for the process is equal to about 5 kg cal. which in turn gives the value of ΔS as about 17 e.u. It seems reasonable to assume that the same entropy change may be involved in the formation of other free radicals by the dissociation of a carbon-carbon linkage, at least in solution in organic solvents. We shall therefore assume that this value is independent of the substituents attached to the two carbon atoms which dissociate from each other. We shall further assume that over the range of temperatures necessary in the extrapolations to be employed the value of ΔS is essentially independent of temperature; we may thus calculate ΔF°_{298} from ΔF at some higher temperature by the approximate equation

$$\Delta F^\circ_{298} = \Delta F^\circ_T + 17(T - 298).$$

Various methods may be employed for estimating ΔF°_T at different temperatures; none of these methods are particularly accurate and the estimates are certainly in error by as much as ± 1.0 kg cal. Such errors, however, are not serious since Ziegler's results show that variations in ΔF and ΔH of as much as 1 or 2 kg cal. may occur due to the nature of the solvent. Therefore, all the values with which we are dealing in this paper may be regarded as uncertain within at least ± 1 kg cal. In spite of their approximate nature, however, we believe that a comparison of all the quantitative facts now available may be of some service in connection with various theories which have been developed on the effect of substituents on the energy of binding of one carbon atom to another.

In Table I are summarized the calculations based on the assumptions previously mentioned. The table is divided into two parts. The first deals with the dixanthyl series which has been particularly studied in this laboratory. The facts on which these computations are based have been previously recorded in the papers referred to. The second part of the table deals with what may be called the tetraphenyl series. The information in regard to these compounds and some others has been exceedingly well summarized in Walden's monograph[3] from which the data have been taken. The method of estimating the degree of dissociation in all but one case depends either on a determination of the apparent molecular weight by the freezing point method in some solvent (usually molten naphthalene at 353°K) or by roughly estimating colorimetrically the temperature at which the degree of dissociation is about 1 percent. The method of estimating α is given in the next to the last column of the table. The value of ΔF°_T is given in the final column. The value of ΔF°_{298} is calculated from this value on the assumption of a constant entropy change as previously explained, and the value of ΔH°_{298} is assumed to be 5 kg cal. greater than ΔF°_{298}.

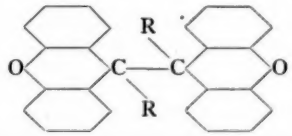
The method of estimating the values for dixanthyl (R = H) requires special comment and the values are very much less certain than the others. The value of ΔF°_{298} was estimated from the fact that the rate of oxygen absorption at 483°K was approximately the same as that for dibutyldixanthyl at 298°K.[4] This rate was presumably a measure of the rate of dissociation of the free radical since this has been proved to be the case with the alkyl derivatives (Conant and Evans). Taking the value of the unimolecular rate constant as 10^{-2} and E as 35 kg cal. (the value found for dimethyldixanthyl), the value of the constant for the rate of dissociation at 298° may be estimated as 10^{-11}. If we further assume that the rate of association of a series of related free radicals is nearly independent of their structure, we may estimate that the value of K (the dissociation constant) for dixanthyl is 10^9 less than for dibutyldixanthyl (since the rate constant of dissociation of the latter is 10^{-2}). The value of ΔF°_{298} of dissociation of dixanthyl may be estimated therefore as 12.3 kg cal. greater than the value for ΔF°_{298} for dibutyl dixanthyl; this gives $13.4 + 12.3 = 25.7$. This value is, of course, a very rough estimate based on several assumptions which are probably only approximately valid.

In connection with Table I it should be noted that the standard state is taken as that of a

[3] P. Walden, *Die Chemie der Freien Radikale.*

[4] J. B. Conant and B. S. Garvey, Jr., J. Am. Chem. Soc. **49**, 2084 (1927); J. B. Conant and M. W. Evans, J. Am. Chem. Soc. **51**, 1932 (1929).

TABLE I. *Estimated values of ΔF and ΔH of dissociation.*

R	$\Delta F°_{298}$ kg cal.	$\Delta H°_{298}$ kg cal.	Method of estimating α	$\Delta F°_T$ kg cal.
(a) Dixanthyl Series of General Formula				
				
C_6H_5 } $C_6H_4CH_3$ }	3.6	8.6	m.w. at 353°	2.7
ClC_6H_4	3.9	8.9	m.w. at 353°	3.0
$(CH_3)_2CH$	qualitatively estimated to be about the same as C_6H_5			
$C_6H_5CH_2$	11.5	16.5	color. (α=.01 at 373°)	10.2
n. C_3H_7 } *n.* C_4H_9 }	13.4	18.4	color.(α=.01 at 433°)	11.1
CH_3 } C_2H_5 }	15.5	20.5	color.(α=.01 at 483°)	12.4
H	25.7*	30.7*	458°* (O_2 absorption)	
(b) Tetraphenyl Series of General Formula $(C_6H_5)_2C(R)—C(R)(C_6H_5)_2$				
C_6H_5	5.5†	10.5†	m.w. at 353°	4.6
α $C_{10}H_7$	1.6	6.6	m.w. at 301°	1.6
β $C_{10}H_7$	3.9	8.9	m.w. at 353°	3.0
p. $CH_3OC_6H_4$	3.7	8.7	m.w. at 326°	3.2
o. $CH_3OC_6H_4$	3.4	8.4	m.w. at 326°	2.9

* See text for explanation of method of calculation.

† Direct colorimetric equilibrium measurements of Ziegler (Ann. **373**, 163 (1929)) give ΔF_{293} 5.3–6.8 and ΔH 10.5–12.0, from which $T\Delta S$=5 and ΔS=17 e.v., the values used in the other calculations in this table as explained in text.

hypothetical supercooled liquid of such a nature that it forms an ideal solution with the solvents in question. The interesting question of the relation between the values of ΔF and ΔH referred to this basis and referred to the gaseous state we prefer to leave open at present. Whether or not a large correction would have to be made for the difference in the energy effects of solvation of the free radical and ethane seems to us still somewhat uncertain. It is conceivable that a solvation phenomenon is involved in the formation of the free radicals. If this is not the case, however, the correction from our standard state to the gaseous state would probably not exceed a few kg cal. At all events, the numbers which are given in Table I may be used for predicting the behavior of organic compounds in a variety of solvents including, in the case of liquid substances, the pure liquids themselves.

The results given in Table I enable us to estimate the effect of various substituents on the tightness of the carbon-carbon linkage. If such effects are approximately additive we may deduce from the data of Table I the effect caused by the replacement of a single hydrogen atom in ethane by a single group. The difference in the dixanthyl series between phenyl and hydrogen is 22 kg cal. This refers to the difference caused by the replacement of the *two* hydrogen atoms of dixanthyl by *two* phenyl groups. Therefore, the effect for a single phenyl group may be estimated as 11 kg cal. In a similar way the other values of Table II are obtained from Table I. It is very interesting that if we take the value for phenyl as 11 and the observed value for ΔH of dissociation of hexaphenyl ethane (10.5) we may estimate the heat of dissociation of the carbon atoms in ethane as $6\times11+10.5=76.5$ kg cal. This is in excellent agreement with the most probable values determined from thermal data.

TABLE II. *Estimated values of effect of substituent groups on heat of dissociation of the ethane linkage.*

Substituent *R*	Change in ΔH_{298} of dissociation of ethane caused by replacement of one hydrogen atom by *single* group (kg cal.)
Methyl, ethyl (CH_3-, C_2H_5-)	−5
Higher normal alkyl groups (e.g., C_4H_9-)	−6
Sec. and tert. alkyl groups (e.g., $(CH_3)_2CH-$)	−11
Phenyl (C_6H_5-)	−11
Benzyl ($C_6H_5CH_2-$)	−7
Alpha-naphthyl (α $C_{10}H_7-$)	−13
Beta-naphthyl (β $C_{10}H_7-$)	−12
p. Methoxyphenyl (*p.* $CH_3OC_6H_4-$)	−12

When a value of 76 is taken for the heat of dissociation of ethane itself and the values for the single groups given in Table II it is interesting to predict the heat of dissociation of certain compounds which cannot at present be measured. Tetraphenylethane has a value of 32 and pentaphenylethane 21. The value for the latter compound is about that of dimethyldixanthyl and the

value for the tetraphenyl compound somewhat greater than that of dixanthyl itself. One would predict that the pentaphenyl compound should give some evidence of dissociation when heated and the tetraphenyl compound probably would not. This is indeed the case,[5] as has been known for some time. On the other hand, hexamethyl-ethane may be calculated as having a value of $\Delta H°_{298}$ of dissociation of 46 kg cal. This is such a large value that it seems unlikely that this compound would show any evidence of dissociation between the central carbon-carbon linkage even at a fairly high temperature. As a matter of fact, cracking experiments in this laboratory have shown that the compound decomposes around 500° but with the formation of methane and other products; there is no evidence of a cleavage of the central carbon-carbon linkage.

The close similarity between the secondary and tertiary alkyl groups on the one hand and the aryl groups on the other has been frequently referred to in papers from this laboratory. The behavior of tetracyclohexyl-diphenyl-ethane recently prepared by Marvel[6] is further evidence in this direction. Although this compound does not form any measurable quantity of free radical in solution, its reactions indicate clearly that a small amount of dissociation takes place.

In the calculation of ΔF of dissociation for dixanthyl itself, it was assumed that the rate of association of all free carbon radicals was approximately the same. There are a great many qualitative facts in the literature which make this assumption probable. The rate of dissociation of ethanes has been measured in two instances. In the case of hexaphenyl ethane itself the work of Ziegler[7] indicates that the heat of activation of the dissociation reaction is almost the same as that of $\Delta H°$ for the process. In other words, the association reaction has almost no heat of activation. The results in the dixanthyl series point in the same direction. The heat of activation of the dissociation of dimethyl-dixanthyl and diethyl-dixanthyl, for example, is about 30 kg cal. and the value for di-*n*-butyl-dixanthyl is about 26. A comparison of these numbers with the values of $\Delta H°_{298}$ in Table I indicates a heat of activation for the association reaction of 14 to 8 kg cal. The measurements are not sufficiently accurate to make these numbers very significant, but it seems extremely probable that the heat of activation of the association reaction in both hexaphenylethane and dixanthyl is small. If this is in general the case, it is clear that the values of the heat of dissociation will give us some information in regard to the heat of activation for the dissociation process in a variety of compounds. Where the value of $\Delta H°$ is less than 12, we may expect clear evidence of the dissociation by means of the color and the peculiar reactions such as rapid oxygen absorption. Where the values run from 15 to 20 a slow oxygen absorption may be expected as well as a reaction with sodium amalgam. The speed of these reactions may very often be simply a measure of the rate of formation of the free radical,—as has been shown to be the case in at least two instances. For values of $\Delta H°_{298}$ of dissociation between 20 and 30, oxygen absorption or decomposition with cleavage of the carbon-carbon linkage may be expected to take place when the compound is heated to 450 or 550°K. On the other hand, with values as high as 46 kg cal. it seems quite clear that other modes of decomposition might take place before the cleavage of the two central carbon atoms occurs. It would, of course, be a matter of great interest to have available such substances as hexaisopropylethane or even tetraisopropyl-diethylethane. These compounds should undergo appreciable dissociation at room temperature. Unfortunately, all attempts to prepare these compounds or substances from which they might be prepared have hitherto failed.

In conclusion it may be mentioned that no account has been taken in this work of the effect of unsaturated groups on the ease of dissociation of the carbon-carbon linkage. There is a mass of qualitative evidence to show the effectiveness of such groups but the data did not lend themselves to the estimations which have been made.[8] Similarly the interesting question of the difference be-

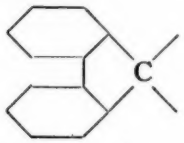
[5] Reference 3, p. 75.

[6] Marvel, J. Am. Chem. Soc. **52**, 2976 (1930).

[7] Conant and Evans, reference 4 and Ziegler, Ann. **479**, 277 (1930).

[8] See for example: Davis and Marvel, J. Am. Chem. Soc. **53**, 3840 (1931).

tween two phenyl groups and the phenylene group



has been left untouched. The phenylene group is much less effective in promoting dissociation than two phenyl groups, whereas the dixanthyl group is somewhat more effective. We may estimate roughly the effect on ΔH°_{298} for these two *divalent* groups as 18 and 23, respectively. These numbers are to be compared with 22 for the corresponding two phenyl groups. Among the facts which any theory in regard to the dissociation of the carbon-carbon linkage must explain is the difference in these numbers.

I should like to express my indebtedness to my colleague Professor H. E. Bent with whom I have often had the pleasure of discussing the problems considered in this paper.

The Thermal Dissociation of Cyanogen into Cyanide Radicals

G. B. KISTIAKOWSKY AND H. GERSHINOWITZ, *Harvard University*

(Received May 8, 1933)

The thermal dissociation of cyanogen into cyanide radicals around 1200°C has been studied. Determining the variation of CN concentration with temperature by the intensity of absorption bands, the heat of dissociation 77±4 kg cal. has been obtained. With this quantity the heat of dissociation of hydrogen cyanide into hydrogen atoms and cyanide radicals is calculated as 94.5±4 kg cal. By the use of existing thermochemical data these quantities are shown to be the most probable values for the energies of the C−C and C−H bonds, respectively. The heat of sublimation of carbon is calculated as 154±3 kg cal.

THERE exists at present considerable difference of opinion as to the correct values for the energies of the carbon-carbon and carbon-hydrogen bonds,[1] the heat of sublimation of carbon[2, 3] and the heat of dissociation of nitrogen.[4] An experimental determination of the heat of dissociation of cyanogen into two cyanide radicals would make possible, if not an exact determination, at least a closer estimate of these magnitudes. There have, however, been no direct measurements of this dissociation energy. On the ground of a relation between electron affinity and heats of dissociation Lederle[5] has calculated a value of 61 kg cal. Mooney and Reid[6] have studied the photochemical dissociation of cyanogen and have indirectly obtained an upper limit for the heat of dissociation into two normal CN radicals.

Therefore, when it was found that cyanogen gas heated to 1000°C showed CN bands in absorption, it was decided to attempt a determination of the heat of thermal dissociation by a method originally used by Franck and Grotian and others[7] for the reaction $Hg_2 \rightarrow 2\,Hg$, and by Bonhoeffer and Reichardt[8] for the reaction $2\,H_2O + O_2 \rightarrow 4\,OH$. This method consists essentially of taking the absorption spectra of cyanogen at various pressures and temperatures, matching absorption bands of equal intensities, assuming that this denotes equal pressures of CN, and calculating the heat of the reaction by means of the van't Hoff isochore.

EXPERIMENTAL

The cyanogen was prepared in an all glass apparatus by dropping a concentrated solution of potassium cyanide into 200 g of copper sulfate in 400 cc of water. The gas evolved passed through a calcium chloride tube and was collected in a trap cooled by a mixture of carbon dioxide snow and ether. It was found that the yield of cyanogen could be considerably improved by keeping the pressure in the apparatus down to about 20 mm of mercury by means of a water pump. Because the vapor pressure of cyanogen at −80°C is 8 mm it was not advisable to keep the pump running continuously. Therefore the system was evacuated at the beginning and then at ten minute intervals, in order to draw off the more volatile impurities (nitrogen and carbon dioxide) which slowly accumulated and built up the pressure. The potassium cyanide was added at a rate of about 2 cc per minute, and when the

[1] Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[2] Vaughan and Kistiakowsky, Phys. Rev. **40**, 457 (1932).

[3] Marshall and Norton, J. Am. Chem. Soc. **55**, 431 (1933).

[4] Kaplan, Phys. Rev. **42**, 97 (1933). By what appears to be a typographical error Kaplan ascribes to Tate and Lozier (Phys. Rev. **39**, 254 (1932)) a corrected value of 9.0 volt-electrons. It is, however, the corrected value of Datta (Proc. Roy. Soc. (London) **A138**, 84 (1932) and Nature **129**, 870 (1932)). The value of Tate and Lozier (8.4±0.5 v.e.) has been adversely criticized by Arnot (Nature **129**, 617 (1932)).

[5] E. Lederle, Zeits. f. physik. Chemie **B17**, 362 (1932).

[6] Mooney and Reid, Nature **128**, 271 (1931) and Proc. Roy. Soc. (Edinburgh) **52**, 152 (1932).

[7] Franck and Grotian, Zeits. f. tech. Physik **3**, 194 (1922). Koernicke, Zeits. f. Physik **33**, 219 (1925). Kuhn and Freudenberg, Zeits. f. Physik **76**, 38 (1932).

[8] Bonhoeffer and Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

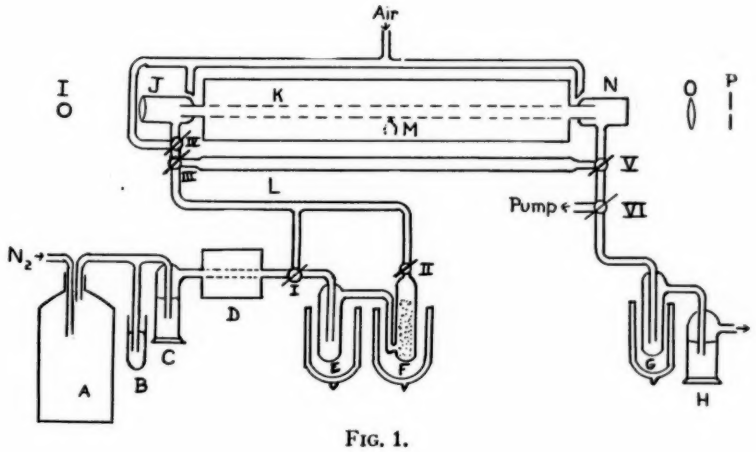


FIG. 1.

calculated amount (about 100 g) had been added the reaction vessel was heated in a water bath for fifteen minutes. When the preparation was made at atmospheric pressure the solution quickly turned black, indicating some reaction with the cyanogen, and the gas evolved contained mostly nitrogen and carbon dioxide. At reduced pressure the solution remained greenish and almost pure cyanogen was obtained. To remove the less volatile impurities such as water and hydrogen cyanide the cyanogen was twice distilled at $-35°C$ and collected at $-80°C$.

Fig. 1 shows the experimental set-up. Since cyanogen slowly decomposes at the temperatures employed in the present work, it was necessary to use a flowing gas system. This was accomplished by adding to nitrogen known partial pressures of cyanogen and passing the mixture through the furnace at atmospheric pressure. Nitrogen from a tank entered a twenty liter bottle *A*, which acted as a barostat, passed through a wash bottle *C*, containing concentrated sulfuric acid, and then through a furnace *D*, which was packed with activated copper filings heated to 250°C, thus removing the little oxygen present in tank nitrogen. The purified gas then passed through the wash bottle *E*, which contained cyanogen at a temperature at which its vapor pressure was about 30 percent greater than that desired.[9] The gases entered next the vessel *F*, filled with glass wool and maintained at a temperature that gave the desired vapor pressure of cyanogen. Frequent observations showed that considerable amounts of cyanogen condensed in *F*, thus proving that saturation was obtained.

E and *F* were maintained at the desired temperatures by ether cooled by carbon dioxide snow contained in large Pyrex Dewar tubes. By hand regulation these baths could be kept constant ($\pm 0.05°C$) for more than a half hour with gas flowing through the system. The temperature in *E* was read by a toluene thermometer, that in *F* by a triple copper constantan thermocouple and a Leeds and Northrup thermocouple potentiometer. This thermocouple was calibrated against the standard tables of Southard and Andrews[10] at the freezing point of mercury and the sublimation point of carbon dioxide. The correction curve was a straight line that passed through the origin. The maximum correction necessary was 50 parts in 2500; at the freezing point of mercury the correction was 23 parts in 1450. According to the discussion of Southard and Andrews the assumption of linear correction would introduce no error, especially since the desired accuracy was only $\pm 0.05°C$.

The gases then entered the furnace. The latter was made of a Sillimanite tube 2.54 cm by 152.6 cm, 132.6 cm of which was closely and evenly wound with chromel A ribbon, 0.05 ohm per foot resistance. The total resistance of the winding was two ohms. Alundum cement served to keep the windings separated and to hold the wire tightly against the wall of the tube. At the center

[9] The vapor pressure of cyanogen as a function of temperature has been determined by Perry and Bardwell, J. Am. Chem. Soc. **47**, 2629 (1923).

[10] Southard and Andrews, J. Frank. Inst. **207**, 323 (1929)

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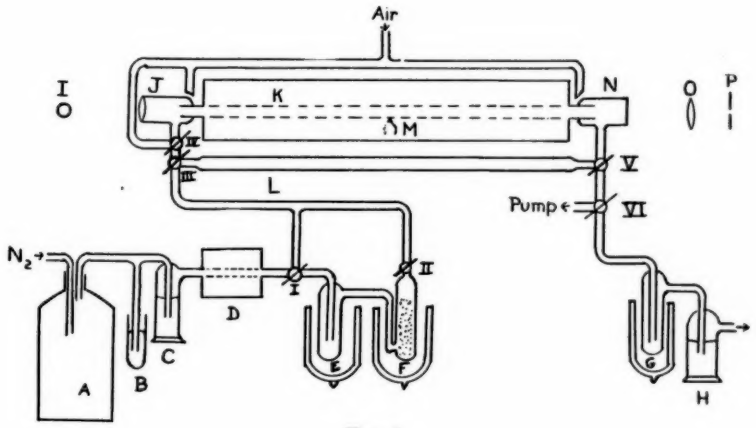

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calculated amount (about 100 g) had been added the reaction vessel was heated in a water bath for fifteen minutes. When the preparation was made at atmospheric pressure the solution quickly turned black, indicating some reaction with the cyanogen, and the gas evolved contained mostly nitrogen and carbon dioxide. At reduced pressure the solution remained greenish and almost pure cyanogen was obtained. To remove the less volatile impurities such as water and hydrogen cyanide the cyanogen was twice distilled at $-35°C$ and collected at $-80°C$.

Fig. 1 shows the experimental set-up. Since cyanogen slowly decomposes at the temperatures employed in the present work, it was necessary to use a flowing gas system. This was accomplished by adding to nitrogen known partial pressures of cyanogen and passing the mixture through the furnace at atmospheric pressure. Nitrogen from a tank entered a twenty liter bottle *A*, which acted as a barostat, passed through a wash bottle *C*, containing concentrated sulfuric acid, and then through a furnace *D*, which was packed with activated copper filings heated to 250°C, thus removing the little oxygen present in tank nitrogen. The purified gas then passed through the wash bottle *E*, which contained cyanogen at a temperature at which its vapor pressure was about 30 percent greater than that desired.[9] The gases entered next the vessel *F*, filled with glass wool and maintained at a temperature that gave the desired vapor pressure of cyanogen. Frequent observations showed that considerable amounts of cyanogen condensed in *F*, thus proving that saturation was obtained.

E and *F* were maintained at the desired temperatures by ether cooled by carbon dioxide snow contained in large Pyrex Dewar tubes. By hand regulation these baths could be kept constant ($\pm 0.05°C$) for more than a half hour with gas flowing through the system. The temperature in *E* was read by a toluene thermometer, that in *F* by a triple copper constantan thermocouple and a Leeds and Northrup thermocouple potentiometer. This thermocouple was calibrated against the standard tables of Southard and Andrews[10] at the freezing point of mercury and the sublimation point of carbon dioxide. The correction curve was a straight line that passed through the origin. The maximum correction necessary was 50 parts in 2500; at the freezing point of mercury the correction was 23 parts in 1450. According to the discussion of Southard and Andrews the assumption of linear correction would introduce no error, especially since the desired accuracy was only $\pm 0.05°C$.

The gases then entered the furnace. The latter was made of a Sillimanite tube 2.54 cm by 152.6 cm, 132.6 cm of which was closely and evenly wound with chromel A ribbon, 0.05 ohm per foot resistance. The total resistance of the winding was two ohms. Alundum cement served to keep the windings separated and to hold the wire tightly against the wall of the tube. At the center

[9] The vapor pressure of cyanogen as a function of temperature has been determined by Perry and Bardwell, J. Am. Chem. Soc. **47**, 2629 (1923).

[10] Southard and Andrews, J. Frank. Inst. **207**, 323 (1929)

TABLE I.

Distance from center in cm	60	40	30	20	10	0	10	20	30	40	60
Temperature °C	1039	1098	1098	1093	1098	1098	1094	1095	1095	1076	1070
Temperature °C	1200	1235	1240	1236	1248	1246	1248	1242	1248	1240	1235

of the furnace a platinum-platinum-rhodium thermocouple was cemented onto the wall of the tube between two turns of the ribbon. The wired part of the tube was packed in Sil-o-cel bricks. To the 10 cm of the tube sticking out at each end were affixed short lengths of 32 mm Pyrex tubing, J and N, by means of porcelain cement made gas tight by coating it with de Khotinsky cement. The cement was kept cold by air blasts. To the ends of the glass tubes were affixed, also with de Khotinsky cement, windows, to J a quartz lens and to N a piece of optically plane quartz. For reasons that will be given below a satin walled quartz tubing of 3/4 inch outside diameter and the length of the furnace was used as a lining, so that the hot gases did not come in contact with the Sillimanite.

The thermocouple was calibrated to give directly the temperature inside the furnace by plotting its e.m.f. readings against the temperature of a movable carbon block, with a conical hole in it, as read by a Leeds and Northrup optical pyrometer with no windows in the way. This calibration was carried out over a range of 300° with an uncertainty of not more than ±3° at the extreme limits. The temperature gradient in the furnace could be obtained by moving the block back and forth. It was found that for a range of 60 cm in the center of the tube the temperature was constant (±3°C). Then it dropped off slowly until at the ends there was a sharp drop. Table I shows the temperature distribution in the furnace. To reach a temperature of 1250°C a current of about 22 amperes was necessary. It took about six hours to heat the furnace to a steady temperature but when equilibrium was reached the temperature would stay constant (±3°C) for long intervals of time.

By turning the three way stopcock III the mixture of nitrogen and cyanogen could be passed through the bypass L until it and the furnace were in the state desired. By turning I the furnace could be flushed with nitrogen and by turning IV it could be thoroughly cleansed of all oxidizable matter by passing air. After flowing through the furnace (or L) the gases passed through the cold trap G and three wash bottles H containing potassium hydroxide solution.

Two electronic transitions from the normal state of cyanide radicals are known, one giving rise to bands in the red ($^2\Pi \rightarrow {}^2\Sigma$), the other to bands in the near ultraviolet ($^2\Sigma^* \rightarrow {}^2\Sigma$). Both represent dipole radiation and thus the ultraviolet bands, having higher frequency, may be expected to be more intense. This transition was therefore used in the present work. On the plates obtained only the O→O band at 3883A was sufficiently intense. A tungsten lamp can be conveniently used to furnish the continuous background at this wave-length.

The light source I, a 500 watt G. E. tubular projection bulb, was placed at the focus of the lens J so that parallel light passed through the furnace, reducing reflection from the walls. The lens O focussed this beam on the slit P of a Hilger E-1 quartz spectrograph. An exposure of thirty seconds was necessary.

For the accurate matching of bands equal intensities of background were quite essential. The light source was very constant since it operated on a regulated 110 volt line. Therefore it was only necessary to make equal the times of exposure. For this purpose the snap of a camera shutter, adjusted for a time exposure, was attached to a piece of laminated iron which hung above the core of an electromagnet. The leads of the electromagnet were connected to the 110 volt line through a rotating commutator driven by a Telechron motor. The commutator was adjusted to give two current impulses thirty seconds apart. The first of these opened, the second closed the shutter.

To make more certain equality of background the bands to be compared were taken on the same plate, which insured equal developing and fixing. Therefore from fifteen to twenty exposures were taken on each plate, at two different temperatures and at pressures determined by preliminary

experiments to give approximately equivalent absorption, and the resulting bands were matched.

Procedure and Results

It was originally intended to run the cyanogen through the Sillimanite tube. When this was done the CN bands were observed only in the first two runs. Thereafter four strong atomic lines and one diffuse band were obtained but the CN band was no longer on the plate. Using higher temperatures and higher pressures of cyanogen resulted in the formation of carbon in the furnace and its consequent blocking. The absorption lines appeared only when cyanogen was run through the furnace, not when blank runs were made with pure nitrogen. The furnace was cleaned (after oxidation with air) and a reddish brown powder was scraped off the walls. Upon analysis this proved to be an oxide of iron. The wave-lengths of the absorption lines were determined and they were identified as being due to copper (3274A and 3248A) and silver (3383A and 3281A). The weak band (3778A) could not be identified. It was obvious that the hot cyanogen was reducing the metallic compounds present in the tube as impurities and that the resulting metals were catalyzing the reaction $C_2N_2 \rightarrow 2C + N_2$. Therefore the quartz tubing described above was introduced as a lining for the furnace. During the rest of the research no further trouble from this source was encountered.

It was found that pressures of cyanogen higher than 350 mm caused a deposit to form on the cold window. This deposit sublimed upon heating and was probably para-cyanogen. A copper diaphragm inside the glass tube in front of the window helped reduce this polymerization, but in order to avoid frequent removal of the window for cleaning it was found most convenient to work at lower pressures and higher temperatures. Since there were no stresses on the quartz tube, which was evenly supported along its entire length, prolonged heating at 1250°C did not result in any damage. The amount of carbon deposited in the furnace after the quartz tubing was introduced was negligible, and since it is known[11] that cyanogen does not polymerize above 800° there was no interference from side reactions.

To determine the effect of the rate of flow through the furnace upon the intensity of the CN bands, nitrogen with a constant partial pressure of cyanogen was sent through the furnace at various speeds. When the linear rate of flow was less than 0.2 or greater than 4 cm per second the intensity of the band was diminished. Rates from 0.5 to 3 cm per second resulted in unchanging intensities. A velocity of 1 cm per second was taken as most convenient. By taking spectra at intervals of three, five, ten and fifteen minutes with the gas flowing at the rate of 1 cm per second it was demonstrated that the gas in the furnace reached a constant composition five minutes after the flow was started. However, to give a margin of safety, the shortest interval used was ten minutes.

For technical reasons the work was limited to temperatures and pressures at which the absorption by CN radicals is quite weak. The bands on the plates consisted actually of only the head of the P branch (see Fig. 2), the remainder being

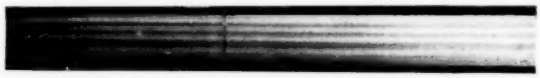

FIG. 2a. Shows a typical absorption band, $T = 1250°C$, $P(C_2N_2) = 100$ mm.

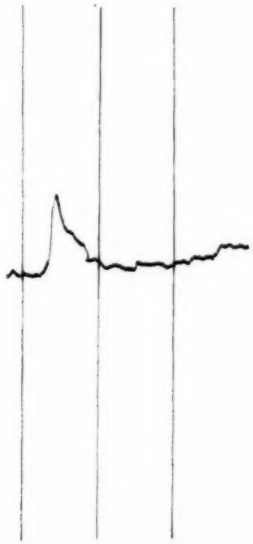

FIG. 2b. The microphotometric record of this band showing the fine structure.

[11] Troost and Hautefeuille, Comptes Rendus **66**, 795 (1868).

too faint to be used for comparison. This circumstance can introduce a serious error if the rotational energy of the quantum states that give rise to lines forming the head of the band is considerably higher than the mean energy. By means of the data given by Weizel[12] this energy was calculated and found to be slightly lower than the mean thermal rotational energy at 1400°–1500°K. Therefore the variation of the intensity of the band head can be taken as a measure of CN concentration.

Since the pressure of the cyanogen could be varied much more easily than the temperature of the furnace, on each plate the spectra were taken at only two temperatures, with from six to ten pressures corresponding to each. Then the bands taken at one temperature were compared with the others and those of equal intensity matched. At first the plates were run through a recording microphotometer, but it was soon found that the eye could distinguish variations to which the microphotometer was insensitive. This agreed with the experience of Bonhoeffer and Reichardt.[8] Therefore the bands were matched entirely independently by three observers. There was unanimous agreement upon eight pairs. Values of ΔH calculated from several pairs concerning which there was disagreement were distributed equally on both sides of the values obtained from the other eight, showing that the pressure intervals had been too great.

By combining the equation for the equilibrium constant $K=P^2(\mathrm{CN})/P(\mathrm{C_2N_2})$ with the van't Hoff isochore $d\ln k/dT=\Delta H/RT^2$ and assuming that $P(\mathrm{CN}<<P(\mathrm{C_2N_2})$ and that ΔH is constant over the temperature range covered, values of ΔH are easily calculated from the matched bands. Table II gives the results.

To obtain the true heat of dissociation from the above, it is necessary to bring in a correction taking care of the gradually falling temperature at the ends of the furnace.[8] In the present case the temperature was sufficiently constant throughout the major part of the furnace to make this correction negligible in comparison with other sources of error.

To reduce the observed ΔH to ΔH at 0°K it is necessary to calculate the specific heats of

[12] Weizel, *Bandenspektren*, p. 370. Leipzig, 1931.

TABLE II.

T°C	P (mm)	ΔH	T°C	P	ΔH
1124	337	76.5 kg cal.	1202	60.6	72.5 kg cal.
1171	137.4		1238	33.6	
1124	147.4	84	1202	64.8	81
1171	55.2		1238	33.6	
1138	425	73	1202	83.7	70
1228	89.3		1238	47.3	
1202	102.3	85.5	1202	74.0	74
1229	60.6		1238	40.5	

Arithmetic mean $=77\pm4$

cyanogen and cyanide radicals. Rotation and translation were taken as classical and the oscillations considered harmonic. Cyanogen has seven vibrational degrees of freedom but due to its symmetry it has only five distinct frequencies. These frequencies were obtained from data on the infrared absorption[13] and Raman spectra[14] of liquid cyanogen, and were distributed as follows. The three longitudinal vibrations were taken as 2336, 2150 and 860 $\mathrm{cm^{-1}}$; 756 and 512 $\mathrm{cm^{-1}}$ were considered the deformation oscillations, each being double. The specific heat of cyanogen, assuming a linear structure with only two rotational degrees of freedom, becomes,

$$c_p=(7/2)R+\varphi(2336/T)+\varphi(860/T)+\varphi(2150/T)+2\varphi(756/T)+2\varphi(512/T).$$

The vibrational frequency[12] of CN is 2056 $\mathrm{cm^{-1}}$ and its specific heat,

$$c_p=(7/2)R+\varphi(2056/T)$$

$\varphi(v/T)$ is the Einstein formula for the specific heat of a harmonic oscillator.

By using these values it is found that the total contribution of the integral is only 0.2 kg cal. This was considered negligible, in consideration of the assumptions involved in the calculation of the specific heats. Therefore for the reaction $\mathrm{C_2N_2}\rightarrow 2\mathrm{CN}$, $\Delta H_0=77\pm4$ kg cal.

It was also considered desirable to calculate

[13] Burmeister, Verh. deut. phys. Ges. **15**, 589 (1913).

[14] Petrikaln and Hochberg, Zeits. f. physik. Chemie **B8**, 440 (1930).

the equilibrium pressure of the CN radicals. For this purpose the entropies of cyanogen and of CN are necessary. The first was calculated from the equation given by Mayer, Brunauer and Mayer.[15] To calculate the moment of inertia of cyanogen the C−C distance was taken to be 1.55A as in aliphatic hydrocarbons and the C≡N distance 1.17A, from the spectroscopic value for CN radicals.[12] P_e was taken as 1 and σ set equal to 2. The frequencies were assigned as in the calculation of specific heat.

For CN a similar equation was used with only one term involving frequency and no σ term. Since the normal state of CN is a $^2\Sigma$, $P_e=2$. The practical molar entropies (neglecting nuclear spin) of cyanogen and cyanide radicals, gases at 1500°K and 1 atm. pressure, are then $38.8R$ and $28.3R$, respectively. On substituting in the proper thermodynamic equations the following data were obtained. $\Delta F°1500°K=22$ kg cal.; $K=7\times10^{-4}$; and for $P(C_2N_2)=100$ mm, $P(CN)=0.3$ mm. This pressure appears to be of a reasonable magnitude considering the length of the furnace used and the absorption intensity obtained.

Discussion and Conclusions

From a study of the ultraviolet absorption spectrum, Mooney and Reid[6] obtain a value of 154 kg cal. for the heat of photochemical dissociation of cyanogen. The excitation energy of a CN radical ($^2\Sigma^*\rightarrow{}^2\Sigma$) is 74 kg cal. (3.2 v.e.).[12] If, therefore, we assume that the photochemical dissociation produces one excited and one normal CN radical, we get 80 kg cal. for the heat of dissociation into normal products. This is in good agreement with our value of 77±4 kg cal. which makes unnecessary the assumption of vibrating CN radicals which Mooney and Reid invoked to explain the disagreement with existing thermochemical data. Lederle's[5] theoretical calculation of the heat of dissociation from electron affinity gives 61±3 kg cal. His method has been very severely criticized by Kuhn,[16] who claims that the correct order of magnitude is all that can be expected from it.

For the calculation of the heat of dissociation of hydrogen cyanide into hydrogen atoms and cyanide radicals we have now the following data:

	ΔH
$(1/2)C_2N_2\rightarrow CN$	+ 38.5±2 kg cal.
$HCN+(9/4)O_2\rightarrow\frac{1}{2}H_2O+CO_2+\frac{1}{2}N_2$	−159±1[17]
$\frac{1}{2}N_2+CO_2\rightarrow\frac{1}{2}C_2N_2+O_2$	+130±1
$\frac{1}{2}H_2O\rightarrow\frac{1}{2}H_2+\frac{1}{4}O_2$	+ 34
$\frac{1}{2}H_2\rightarrow H$	+ 51[18]
$HCN\rightarrow H+CN$	94.5±4 kg cal.

There now remains the question as to whether the energies of the carbon-carbon and carbon-hydrogen bonds are approximately independent of the compound in which they occur. While this principle is exceedingly doubtful in the case of highly phenylated compounds where there is considerable steric hindrance, it seems quite plausible for aliphatic hydrocarbons and their usual derivatives. To determine whether the above values apply to aliphatic hydrocarbons the following equations can be set up:

	ΔH
$C\ g+2H_2\rightarrow CH_4$	− 18.5 kg cal.[19]
$CH_4\rightarrow C$ vapor$+4H$	+378 kg cal.[20]
$4H\rightarrow2H_2$	−205 kg cal.[15]
$C\ g\rightarrow C$ vapor	+154 kg cal.

[15] Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 38 (1933), Eq. (4).

[16] Kuhn, Zeits. f. physik. Chemie **B19**, 217 (1932).

[17] All thermochemical data are from Landolt-Bornstein unless otherwise noted.

[18] Weizel, reference 12, p. 249.

[19] Egloff, Schaad and Lowry, J. Phys. Chem. **34**, 1617 (1930).

[20] Calculated on the assumption that the energy of the C−H bond is 94.5 kg cal.

If these data are now set into the equations for ethane we should be able to get a value for the energy of the carbon-carbon bond.

Thus

	ΔH
$2C\ g+3H_2\rightarrow C_2H_6$	− 23 kg cal.[21]
$6H\rightarrow 3H_2$	−308[18]
$2C\ vapor\rightarrow 2C\ g.$	−309
$C_2H_6\rightarrow C-C+6H$	+563[20]
$2C\ vapor\rightarrow C-C$	− 76 kg cal.

This value checks better than should be expected with the 77 ± 4 obtained for the heat of dissociation of cyanogen. Hence, it seems very probable that the principle of constancy of bonding energies is sufficiently valid to justify assigning, to ordinary compounds, as the energy of the carbon-carbon bond 77 kg cal. and that of the carbon-hydrogen bond 94.5 kg cal.

As an intermediary quantity in the above calculation we found 154. kg cal. for the heat of sublimation of carbon. The quantity can now be calculated in several other ways. According to the valence theory of Heitler and London[22] the carbon atom with a valence of four, as for instance in diamond, must be in the ^5S state. Accordingly the heat of sublimation of carbon should be equal to twice the energy of a carbon bond minus the energy of the transition $^5S\rightarrow{}^3P$. Assuming 1.6 v.e. (37 kg cal.)[12] for the energy of excitation, this would give 116 kg cal. for the heat of sublimation, an improbably low value. However, according to the Hund-Mulliken theory[23] carbon compounds in the normal state can dissociate directly into ^3P-atoms. Therefore we would get 154 kg cal. for the heat of sublimation.

For the heat of dissociation of CO Weizel[12] gives 10.3 v.e. (234 kg cal.). Therefore we have:

	ΔH
$CO\rightarrow C\ vapor+O$	+234 kg cal.
$C\ g+\frac{1}{2}O_2\rightarrow CO$	− 22
$O\rightarrow\frac{1}{2}O_2$	− 59[12]
$C\ g\rightarrow C\ vapor$	+153 kg cal.

Mulliken,[24] on the other hand, gives 10.0 volts for the dissociation energy of CO which would give 147 kg cal. for the heat of sublimation. This is equal to the corrected value of Fajans[25] calculated from pressure-temperature data. Marshall and Norton,[3] however, point out that the temperatures used may be as much as 200° too high, which would make the calculated values of the heat of sublimation too low.

There is still another way of calculating the heat of sublimation making use of the heat of dissociation of CN radicals. Herzberg and Heitler[26] have determined 9.7 v.e. as the energy of dissociation of the $^2\Sigma$ CN bond by the Birge-Sponer method. On the basis of the Heitler-London theory they assume that the dissociation products are a ^5S carbon and a ^4S nitrogen. Therefore assuming 1.6 v.e. as the excitation energy of the transition $^5S\rightarrow{}^3P$ we get 8.1 v.e. for the dissociation of $^2\Sigma$ CN into normal atoms. This is the value given by Weizel.[12] Due to the fact that a considerable extrapolation was necessary, under which conditions the Birge-Sponer method gives results that are too high, this value is rather uncertain. By the Hund-Mulliken theory, however, the normal $^2\Sigma$ CN should dissociate into normal atoms. Rejecting Herzberg's analysis of the CN $^2\Sigma$ Mulliken[22] takes a more accurate determination by Birge of the heat of dissociation of the $CN\,^2\Sigma^*$ (6.3 e.v.) and assuming that the excited radical breaks up into ^2D nitrogen and ^3P carbon gets 7.1 v.e. (161 kg cal.) for the dissociation of the $^2\Sigma$ into normal atoms. There is, however, another possibility which Mulliken rejects although stating that it is just as probable, namely the $CN\,^2\Sigma^*$ may yield ^4S nitrogen and ^5S carbon atoms. This gives 8.0 v.e. (185 kg cal.) for the heat of dissociation of $^2\Sigma$ into normal atoms. For the heat of dissociation of nitrogen Kaplan[4] shows that the most recent and most accurate determinations give a mean value of 9.0 ± 0.1 v.e. (208 kg cal.). The use of this value in the following computations will introduce into the heat of sublimation of carbon an uncertainty

[21] Parks and Huffman, *Free Energies of Some Organic Compounds* (Chem. Cat. Co. 1932), p. 60.

[22] Heitler and London, Zeits. f. Physik **44**, 455 (1927); Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[23] Mulliken, Rev. Mod. Phys. **4**, 38 (1932). Hund, Zeits. f. Physik **63**, 719 (1930) and earlier papers.

[24] Mulliken, Rev. Mod. Phys. **4**, 78 (1932).

[25] Fajans, Zeits. f. Elektrochemie **31**, 63 (1925).

[26] Herzberg and Heitler, Zeits. f. Physik **53**, 52 (1929); Herzberg, ibid. **52**, 815 (1929).

of half the magnitude and of opposite sign to that of the energy of dissociation of nitrogen.

	ΔH
$CO_2+\frac{1}{2}N_2\rightarrow\frac{1}{2}C_2N_2+O_2$	+130 kg cal.
$C\ g+O_2\rightarrow CO_2$	− 94
$N^4S\rightarrow\frac{1}{2}N_2$	−104
$CN^2\Sigma\rightarrow C^3P+N^4S$	+185
$\frac{1}{2}C_2N_2\rightarrow CN^2\Sigma$	+ 38
$C\ g\rightarrow C^3P$	+155 kg cal.

If we substitute Mulliken's value of 161 kg cal. for the energy of dissociation of CN we get only 131 kg cal. for the heat of sublimation, which appears to be much too low, indicating that the most probable dissociation products of the $CN^2\Sigma$ are an excited carbon atom and a normal nitrogen.

Thus by four different methods, we get 154±1 kg cal. for the heat of sublimation of carbon. Considering the probable deviations of the thermochemical data used, the most probable value is 154±3 kg cal. By measurements of the loss of weight of carbon rings in vacuo Marshall and Norton[3, 27] calculate the heat of sublimation to be 177 kg cal. In their computations they make use of two doubtful assumptions, first that the accommodation coefficient is unity, secondly that the surface of the carbon ring is equal to the geometric surface. The questionable validity of these assumptions make difficult an interpretation of their data.

Concerning the theoretical values of Vaughan and Kistiakowsky, the Hund-Mulliken theory would point to 5.5 v.e. as the heat of dissociation of C_2 molecules and hence make the lower limits of the calculations the most probable values. The value of 154±3 kg cal. falls within these limits. The consistency of the results obtained by the use of these values for the energies of the C−C and C−H bonds and the heat of sublimation of carbon is a favorable indication of their validity.

Note added in proof: Since the completion of this paper McMorris and Badger[28] have obtained for the heat of combustion of cyanogen a new value of 251.4±1.2 kg cal. In our calculations we have made use of the difference between one-half the heat of combustion of cyanogen and the heat of combustion of hydrogen cyanide. Although Thomsen and Berthelot give different values for each of these quantities, the difference calculated from the two sets of values is the same. Thus it would seem that whatever errors were made in the calorimetric determinations were systematic, and therefore it would not be correct to use the new value for the heat of combustion of cyanogen and the old one for hydrogen cyanide. In an earlier paper Badger[29] announced that he expected to redetermine the heat of combustion of hydrogen cyanide. Until this new value is forthcoming it would seem safest to use the old values of Thomsen and Berthelot which give perfectly consistent results.

In their calculation of the entropy of cyanogen McMorris and Badger make use of a frequency of 240 cm^{-1}. The introduction of this frequency into our calculations would raise ΔH_0 for the reaction $C_2N_2\rightarrow 2CN$ by about 1.4 kg cal. However, there is practically no experimental evidence for the existence of this low frequency and, indeed, its adoption would compel one to regard the Raman line at 756 cm^{-1} as a combination frequency.

[27] We wish to thank Drs. Marshall and Norton for allowing us to see their paper in manuscript.

[28] McMorris and Badger, J. Am. Chem. Soc. **55**, 1952 (1933).

[29] Badger, J. Am. Chem. Soc. **54**, 3528 (1932).

Thermodynamics and the Kinetics of Gaseous Reactions

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IT is commonly recognized that the free energy change of a reaction mechanism gives no information as to the rate of the mechanism. In some cases the heat of the reaction is significant but the really important thing is the heat of activation which bears no relation to the change in energy for the reaction, except that it is usually equal to or greater in magnitude algebraically. This is little more than saying that it is usually a positive quantity. The heat of activation may be obtained (practically) independently of all assumptions, from the temperature coefficient of reaction rate but the rate may not be measured with any greater accuracy than the absolute rate of the reaction, and often with much less accuracy. It would be desirable to be able to estimate heats of activation from measurements of rate at a single temperature and *vice versa*.

The absolute rate of a reaction depends not only upon the heat of activation but upon certain additional terms which are analogous at least to entropies. This is a plausible analogy. If we assume that the energy of activation is required in the formation of an unstable complex, then the greater number of possible states for this complex, the more rapid the reaction. The complete equation for both heat and entropy of activation may be said to define a free energy of activation.

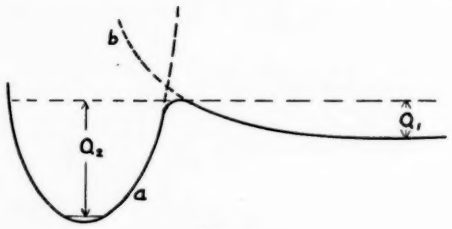

FIG. 1.

We may illustrate the aptness of these thermodynamic, analogies by considering a simple mechanism, the homogeneous bimolecular condensation of two unlike atoms to form a diatomic molecule.

$$A+B=AB. \tag{1}$$

Let us assume for purposes of generality that the potential energy of the molecule is represented by a curve of the type of Fig. 1 with a hump at the point of dissociation. We shall show later that the energy of formation of the molecule in the average vibrational state is

$$\Delta E=Q_1+\tfrac{1}{2}RT-Q_2. \tag{2}$$

By a familiar equation of thermodynamics

$$\ln K=-(\Delta E-RT)/RT+\Delta S/R, \tag{3}$$

where K is the equilibrium constant of (1), which will be expressed in this paper in terms of numbers of molecules per cubic centimeter. For the Eq. (3)

$$\Delta S/R=S_{AB}/R-S_A/R-S_B/R \tag{4}$$

and from quantum statistical theory at unit concentration

$$S_A/R=\ln (2\pi m_1kT/h^2)^{\frac{3}{2}}+5/2, \tag{5}$$

$$S_B/R=\ln (2\pi m_2kT/h^2)^{\frac{3}{2}}+5/2, \tag{6}$$

$$S_{AB}/R=\ln (2\pi(m_1+m_2)kT/h^2)^{\frac{3}{2}} +\ln (8\pi^2IkT/h^2)+\ln (kT/h\nu)+9/2. \tag{7}$$

In the foregoing equations m_1 and m_2 are the masses of the two atoms, I is the moment of inertia of the diatomic molecule, $(m_1m_2/m_1+m_2)r^2$, where r is the distance between centers of the atoms and ν is the characteristic frequency of vibration for the molecule. The other symbols have their usual significance. Eq. (9) does not make any allowance for the change of moment of inertia, or of vibrational frequency in the excited states. These effects could of course be taken care of by more elaborate expressions but the illustration does not lose any significance through the simplification.

Upon substitution from (2) and (5) (6) and (7) in (3) we have

$$\ln K = -(Q_1 - Q_2)/RT + \ln [2^{\frac{1}{2}}\pi^{\frac{1}{2}}(m_1+m_2/m_1m_2)^{\frac{1}{2}}r^2(kT)^{\frac{1}{2}}] - \ln \nu. \quad (8)$$

Now the reaction toward the right is bimolecular and toward the left unimolecular. Hence for the rates of these two opposing reactions we may write

$$R_1 = k_1 n_1 n_2, \quad (9)$$

$$R_2 = k_2 n_3, \quad (10)$$

where n_1, n_2 and n_3 are the concentrations of A, B and AB respectively. Since at equilibrium

$$R_1 = R_2 \quad (11)$$

we have

$$K = k_1/k_2 \quad (12)$$

and we may now write

$$\ln k_1/k_2 = -(Q_1 - Q_2)/RT + \ln [2^{\frac{1}{2}}\pi^{\frac{1}{2}}(m_1+m_2/m_1m_2)^{\frac{1}{2}}r^2(kT)^{\frac{1}{2}}] - \ln \nu. \quad (13)$$

Let us now arbitrarily separate Eq. (13) into two parts

$$\ln k_1 = -\frac{Q_1}{RT} + \ln \left[2^{\frac{1}{2}}\pi^{\frac{1}{2}} \left(\frac{m_1+m_2}{m_1m_2} \right)^{\frac{1}{2}} r^2(kT)^{\frac{1}{2}} \right], \quad (14)$$

$$\ln k_2 = -Q_2/RT + \ln \nu \quad (15)$$

or omitting logarithms

$$k_1 = \left[2^{\frac{1}{2}}\pi^{\frac{1}{2}} \left(\frac{m_1+m_2}{m_1m_2} \right)^{\frac{1}{2}} r^2(kT)^{\frac{1}{2}} \right] e^{-Q_1/RT}, \quad (16)$$

$$k_2 = \nu e^{-Q_2/RT}. \quad (17)$$

When we write

$$R_1 = k_1(n_1n_2) \quad (18)$$

we see that the rate of formation of the molecule AB is put equal to the number of collisions between atoms A and B in which the kinetic energy in the line of centers is greater than Q_1. This is of course plausible. Likewise we may write

$$R_2 = k_2 n_3 = \nu n_3 e^{-Q_2RT}, \quad (19)$$

which is the rate of dissociation of activated molecules, assuming that dissociation takes place at the end of the first vibration as is known to be the case in the phenomenon of predissociation.

The number of collisions calculated in (16) is of course dependent upon the value used for r hence in general we shall need a "steric factor" for "efficiency" of collisions in (16), but the same factor must be introduced in (17) if (13) is to be true. k_1 and k_2 are constants since the probabilities of reactions in collision are not dependent upon the existence of a state of equilibrium but rather determine the equilibrium itself. If the reaction were between two like atoms the symmetry factor of $\frac{1}{2}$ which would appear in the entropy of the diatomic molecule would be identified with the factor $\frac{1}{2}$ in the expression for the number of collisions between like atoms.

At this point we may justify Eq. (2). If we differentiate Eqs. (16) and (17) we obtain

$$d \ln k_1/dT = (Q_1 + \tfrac{1}{2}RT)/RT^2, \quad (20)$$

$$d \ln k_2/dT = Q_2/RT^2. \quad (21)$$

$Q_1 + 1/2RT$ and Q_2 are the heats of activation as defined by Tolman.[1] The heat of activation is taken to be the difference between the average energy of the activated molecules and the average energy of all molecules.

Eq. (19) is interesting since it gives us the rate of a unimolecular reaction, the dissociation of a diatomic molecule in terms of the number of activated molecules and the frequency of vibration. Since ν is large the concentration of activated molecules $n_3e^{-Q_2/RT}$ must be small. The only way activated molecules can be formed accord to Eq. (1) is by collision of A and B and an activated molecule is formed at every collision of A and B which takes place with sufficient violence. That is to say the equations here developed take account only of the two opposing mechanisms postulated in (1). They take no account of the combination of A and B in triple collisions or the activation of the molecule AB by collision with another atom or molecule.

It is not surprising that for an idealized model that the results of simple kinetic theory should agree with thermodynamics. It is important to consider whether the behavior described above may be expected in real molecules. The constancy of the frequency ν at high levels is only possible if

[1] Tolman, *Statistical Mechanics*, Chem. Catalog Co., New York (1927).

the hump in Fig. 1 is very sharp. In this case there is also the possibility of the molecule dissociating by "leaking" through the hump. Aluminum hydride appears to be an example of a molecule with flat hump. Many examples[2] of such humps are to be found in excited states of molecules. It seems likely that the nitrogen[3] molecule in the metastable A state comes to equilibrium with nitrogen atoms by a reversible predissociation mechanism which is of the type (1) discussed above, and for which a constant frequency ν would be significant.

In any event we may say that since the average molecule dissociates with an excess (kinetic) energy kT that the average life period of an activated diatomic molecule is short and of a period comparable to $1/\nu$. It seems probable that the negative temperature coefficient observed in some third order reactions is caused by the decrease in the average life period of some unstable complex with increasing kT, as is predicted by the above reasoning.

The Theory of Unimolecular Reactions

The rate of most unimolecular reactions may be represented by an expression of the form of Eq. (19) where Q_2 is the heat of activation and ν has a value of 10^{11} to 10^{13}, which corresponds roughly to the infrared frequency of the molecule. The heats of activation are usually not very large and in most cases certainly much less than the heat of dissociation to be expected for a bond.

Some years ago the author attempted an explanation[4] of this fact. It seems desirable to restate the ideas presented in that paper in the light of our present knowledge of the behavior of vibrating molecules. The author postulated exactly the mechanism of activation of molecules by collisions which has been discussed at length by Kassel, Rice and others.[5] An N_2O_5 molecule, for example, acquires by collision an energy in excess of the critical energy required for dissociation. This activated molecule has an average life period of the order of 10^{-6} seconds. If collision occurs before this time the molecule will be deactivated but if collision does not occur soon enough the energy will become concentrated in some one bond (probably any one of a number of different bonds) and the molecule dissociates, perhaps at the end of the first vibration as in the case of the diatomic molecule. The author did not discuss the possibility of a decrease in rate at low pressures because it seemed unlikely that this could be observed in the case of nitrogen pentoxide and as a matter of it is only observed at pressures so low that the results are subject to considerable experimental uncertainty. Also he did not consider the possibility of a complete interchange of energy in a collision because at that time it was not known to be either necessary or possible. The case of nitrogen pentoxide is unique in this respect because of the symmetrical structure of the molecule and the possibility of dissociation taking place in various ways. The author considered the molecule as a loose complex of atoms within which energy is transferred by collisions between adjacent atoms.

It seems possible at present to give these ideas a much more precise form in the light of our present knowledge of potential energy curves for molecules.

It seems reasonable to assume that when two adjacent atoms in a complex molecule are separated beyond a certain critical distance that the two portions of the molecule, each rearrange with a decrease in total potential energy and the complete rupture of the bond. Such a rearrangement bears a close analogy to the change to another electronic state that is assumed to take place in predissociation or the Auger effect. This point has been discussed at length by Kassel.[5] This situation would be represented by Fig. (1) if we consider the hump as defined by the dotted lines. The curve b represents a repulsive state for the two parts of the molecule. This comes about through a rearrangement of the valence forces to form two approximately saturated molecules which have very little residual attraction for each other. The hump will now have a sharp peak, and the peak will lie much below the energy of dissociation for the bond. Hence the mechanical frequency of vibration at the peak will not differ greatly from ν_0 the fundamental frequency of the bond.

If the foregoing conditions obtain the rate of

[2] Hulthén and Rydberg, Nature **131**, 471 (1933).
[3] Kaplan, Phys. Rev. **37**, 1407 (1931).
[4] Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).
[5] Kassel, *Kinetics of Homogeneous Gas Reactions*, Chem. Catalog Co., New York (1932).

dissociation will be given by the expression

$$\nu n e^{-Q_2/RT}$$

provided that an equilibrium concentration of molecules is maintained and that dissociation takes place at the end of the first vibration. Even if the equilibrium concentration is not maintained the rate may still be given by the above expression as the following reasoning will show. Since Q_2 is large, corresponding to a high vibrational state there is a high probability that some energy will be transferred to some other part of the molecule at the end of a single vibration. This would mean that the bond would be deactivated at the end of the first vibration and the rate of deactivation must be equal to rate of activation. Now if every activated molecule dissociates the rate of dissociation will be given by the rate of activation and this will of course be unaffected by the fact that the molecules previously activated have dissociated. This is essentially the argument given by the author in his original paper.

The foregoing picture is of course much too simple since we are treating the vibration of a single bond as for a diatomic molecule whereas we are dealing with the complex vibrations of a polyatomic molecule. It seems probable that certain factors need to be introduced which might make the rate less or greater than that given above.

For example, it seems likely that the equilibrium concentration of activated molecules may be maintained owing to the fact that the bond does not break at the end of the first vibration. There may be a probability much less than unity that the molecule will transform from the state a to the state b when it is at the point of intersection. The transformation may take place by leaking through the hump. This possibility has been discussed by Bourgin[6] and there seems to be nothing against it except that it is not known to be required as an explanation. Finally, of course, the expression $e^{-Q_2/RT}$ is the fraction of the total number of harmonic oscillators with energy in excess of a certain critical amount. The fraction of the total number of molecules with vibrational energy in a certain bond in excess of the critical amount may be much different for polyatomic molecules, due to weight factors different from unity for the various energy states.

The number of bonds susceptible of rupture differs in different molecules. It is surprising therefore that the rate of so many unimolecular reactions may be represented by an equation such as (19) with such a small range of values for ν.

Bimolecular Mechanisms

A bimolecular metathesis $A+BB=AB+B$ may be treated by the methods used in discussing the mechanism (1) in the beginning of this chapter, if we assume that the intermediate step in the reaction is the formation of the complex ABB. Eq. (13) should hold but there will now be two steric factors involved in the formation of the complex from $A+BB$ and $AB+B$, respectively, and these factors need not be equal. The kinetic theory is not adequate for the discussion of collisions between complex molecules. The method used here involves the assumption of complex formation. Kassel has discussed the relative merits of the two methods and has shown that they amount to the same thing in the end. The application of thermodynamics seems likely to be of greater utility since it may be possible to calculate the entropy of intermediate complexes, especially when we have more experimental data to give us information about steric factors. The difficulty with the entropy of activation is similar to the difficulty with the heat of activation. The entropy of activation bears no relation to the total entropy change of the reaction. The energy is assumed to be a maximum for the intermediate complex. The entropy of the intermediate complex, however, will in general be neither a maximum nor a minimum nor so far as one can predict any unique value. It seems possible to define the intermediate complex in such a way that the steric factors for the reaction in the two directions will be equal. This result would be apparently an extension of the principle of microscopic reversibility. It is not certain however that this definition would correspond to the unique definition required for the heat of activation.

[6] Bourgin, Proc. Nat. Acad. Sci. **15**, 357 (1929).

The Entropy of a Crystalline Solution of Silver Bromide and Silver Chloride in Relation to the Third Law of Thermodynamics

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With the object of testing experimentally the third law of thermodynamics as applied to crystalline solutions, the chief thermodynamic properties of such a solution of silver bromide and silver chloride have been studied. Measurements described and recorded include: the free energy of formation, obtained from measurements of the e.m.f. of appropriate silver-silver halide electrodes against hydrogen; the heat of formation, from measurements of heat absorbed in dissolving the various phases in a thiosulfate solution; the specific heats between 15°K and 298°K of the pure constituents and the solid solution. The entropy of silver bromide and of silver chloride is calculated from the specific heat curves. The entropy change in the formation of the solid solution at 298°K is calculated from the experimental data and is found to agree with the result calculated statistically. The latter is identical in form and magnitude with the entropy as calculated thermodynamically for an ideal solution, though the heat content and free energy show that the solution is far from perfect. From the specific heat curves it appears that the entropy of mixing persists essentially unchanged in magnitude to the lowest temperature of the measurements, and presumably to the absolute zero. The existence of finite entropies, or entropy differences, at the absolute zero is regarded as established thermodynamically, and the requisite interpretation of statistical ideas to secure concordance with this result is discussed. Finally, although the existence of a valid but limited third law is accepted, and a concise general statement of it suggested, it is pointed out that the "principle of the unattainability of the absolute zero" must be regarded as extra-thermodynamic in character.

THE early formulations of the third law gave rise at once to questions concerning its application to solid solutions. Thus Nernst[1] expressed the opinion that the law, in the form that entropy changes are zero at the absolute zero, is strictly applicable to all condensed systems. Planck[2] and Einstein,[3] however, in addition to adopting the concept of absolute entropy and assigning zero entropy to pure solids at 0°K, took the position that the entropy of mixing must persist to the lowest temperatures. They maintained, therefore, that solid solutions must possess finite positive entropy at the absolute zero.

Subsequently, a number of papers addressed to this question, and the essentially similar problem of the super-cooled liquid or glass, have appeared. A paper by Stern[4] treats theoretically of *crystalline* solutions. Lewis and Gibson[5] discuss generally both solid solutions and glasses, and Pauling and Tolman[6] give a detailed theory for glasses. On the experimental side Gibson and his collaborators[7] have studied glassy solutions of ethyl and methyl alcohols, and pure glycerol glass. Simon and Lange[8] also studied glycerol, carrying the measurements to liquid hydrogen temperatures. As far as we are aware, however, no crystalline solution has previously been investigated experimentally.

Although the essential problem is the same in all cases mentioned above, the crystalline solution presents it in its simplest form theoretically and experimentally. Such systems are clearly visualized as random distributions of the component molecules over the points of a lattice. There is little necessity, in simple cases, for special assumptions relating to the quantum states of the atoms or molecules, since these can

[1] Nernst, Sitzber. Kgl. Preuss. Akad. Wiss. 972 (1913).
[2] Planck, *Thermodynamik*, Veit and Co., Leipzig (1913).
[3] Einstein, Second Solvay Congress, Brussels, 1913; *Rapports*, Paris (1921).
[4] Stern, Ann. d. Physik **49**, 823 (1916).
[5] Lewis and Gibson, J. Am. Chem. Soc. **42**, 1529 (1920).
[6] Pauling and Tolman, J. Am. Chem. Soc. **47**, 2148 (1925).
[7] Gibson, Parks and Latimer, J. Am. Chem. Soc. **42**, 1542 (1920); Gibson and Giauque, J. Am. Chem. Soc. **45**, 93 (1923).
[8] Simon and Lange, Zeits. f. Physik **38**, 227 (1926).

scarcely differ in type from those of pure crystals. This comparative simplicity in physical state may be assumed to be reflected also in the simpler specific heat laws applicable to crystals. This is important practically since it renders the necessary extrapolations to absolute zero less open to question. These advantages seemed to us to warrant experiments designed to test the behavior of some typical crystalline solution with respect to the third law.

We have therefore determined the free energy and heat of formation of a crystalline solution of silver bromide and silver chloride from the pure compounds at 298°K. From these data the entropy of formation of the solution is calculated. We have also measured the specific heats of the pure compounds and the solution in the temperature range from 298°K to 15°K. By extrapolation of these data, in conjunction with the entropy value at 298°K, we have obtained an estimate of this entropy change at the absolute zero. The present paper comprises the results of these studies, together with a discussion of the differences of interpretation which still obtain in this field.

Preparation and Tests of the Solid Solution and Other Materials

The existence of a complete series of solid solutions of the bromide and chloride of silver is well established. Küster[9] prepared such solutions by precipitation from silver nitrate and mixed halide solutions. Monkemeyer[10] prepared them by fusion, and determined the freezing point—composition curve (which shows a minimum at 65 mole percent silver bromide). Wilsey[11] made x-ray photograms of various solutions prepared by fusion, and of each of the pure substances, in powder form. He found each substance to crystallize with the sodium chloride type of lattice, and that the lattice constants of the solutions lie linearly between those of the pure crystals when plotted against mole fraction.

In our own work it was established in numerous preliminary experiments that mixed-crystals of reproducible composition and properties could be most conveniently prepared by precipitation from silver nitrate with mixtures of hydrochloric and hydrobromic acid. Mixtures of solutions of known concentration of these substances were made up by weight, and after shaking for various periods at 25° the weights of the precipitated solid solutions were determined. These data permit the calculation of the composition of the crystals and of the ratio HCl/HBr in the solutions in equilibrium with them. It was ascertained in these experiments that four days shaking at 25° is sufficient to establish equilibrium of the precipitate with the solution even in the extreme cases. For example, in precipitations involving the same quantities the product was the same after four days, whether silver chloride was first precipitated and then the hydrobromic acid added, or the reverse procedure followed.

The character of the material so obtained was further tested in qualitative experiments by comparing microscopically its index of refraction in sodium light with that of silver chloride and silver bromide by means of a series of sulfur-selenium melts of appropriate range. The refractive index of the solution lay between those of the pure substances. No indication of inhomogeneity was found.

The ability of the solid solution to withstand low temperature treatment without appreciable separation into its constituents was also established by tests of its refractive index after prolonged immersion in liquid air. These preliminary tests were fully substantiated in our later work when x-ray photograms[12] were obtained of the solid solution as finally prepared for our measurements and of a sample of the same material taken from the calorimeter after our specific heat measurements, extending to liquid hydrogen temperatures, had been completed. No detectable difference was present. Moreover, the lines of the pure crystals, exposures of which were also made, were entirely absent from the photograms of the solid solution, and the lattice constants of our solutions were closely calculable by interpolation from the constants of the pure substances, as was found by Wilsey with his samples.

[9] Küster, Zeits. f. anorg. allgem. Chem. **19**, 81 (1899).
[10] Monkemeyer, Neues Jahrb. Mineral Geol. Beil. **22**, 1 (1906).
[11] Wilsey, J. Frank. Inst. **200**, 739 (1925).

[12] We are indebted to Dr. W. H. Dore for placing apparatus at our disposal for the x-ray exposures.

The material used in all of our final measurements was prepared in a single batch of about 1.5 moles by precipitation from mixed acids, 1.7 *M* total concentration, with 0.1 *M* $AgNO_3$. The amounts used were calculated from the preliminary experiments to give a solid solution of about 73 mole percent silver bromide, with a concentration ratio (HCl/HBr) of the acids in equilibrium with it of 190. After slowly adding, with vigorous shaking, the silver nitrate to the solution of the acids, the precipitate was allowed to stand, with occasional shaking, for a week at 25° to establish equilibrium. It was then washed repeatedly for another week with 0.1 *M* acid of the equilibrium concentration ratio until freed from detectable amounts of nitrate. The precipitation of the mixed crystals (and the pure substances also) was carried out in dim red light. At no time in any of the subsequent operations or in the experiments themselves were the salts exposed to direct daylight, and only rarely to more than a subdued red light.

A part of the total quantity of the mixed crystals described above was set aside in contact with the equilibrium solution for use in the e.m.f. measurements described later. The remainder, after settling and draining, was dried by evacuation with a mercury vapor pump. Subsequent fusion of samples of material so dried showed a loss in weight of less than 0.03 percent. It is recognized that slight changes in surface composition of the crystals may have been caused by this method of drying. In view of the nearly complete removal of liquid before evacuation, and the rapidity of the evacuation itself, the amounts affected by these changes must have been very small.

The solid solution thus prepared was analyzed by conversion to the chloride by heating in a stream of dry chlorine. Four determinations gave 72.80 ± 0.08 mole percent silver bromide as a mean, in satisfactory agreement with the composition estimated in its preparation. From the standpoint of the entropy change, an equimolal mixture would be preferable. Departure from this ratio was made in order to avoid very large equilibrium ratios of the acids used as electrolytes in our e.m.f. measurements, as increased precautions are otherwise required for accurate work.

Pure silver chloride and silver bromide were prepared in about the same amount and under the same light conditions as the solid solution. The solutions used in these preparations were 0.1 *M*. The precipitated salts were washed with conductivity water until methyl red gave no test for acid. Portions of each were dried by evacuation as described above, the remainder being kept in water.

The Free Energy of Formation of the Solid Solution

We have determined the free energy of formation of the mixed crystals described above from measurements of electromotive force. The cells employed were of the type Ag, AgBr·AgCl (mixed crystals), HCl+HBr (equilibrium ratio), H_2, together with similar cells employing the pure halides with the corresponding pure acids.

The cells and hydrogen generators were of the types described by Lewis, Brighton and Sebastian.[13] The platinum electrodes were of the platinized platinum type with a fairly thin coating of platinum black. The silver electrodes were of spiral form, made in the way described by Randall and Young.[14] It was found convenient to make them six at a time and place them in small glass tubes. These tubes were then heated, evacuated with a mercury vapor pump and sealed. In use, these electrodes were surrounded by the salts described above, instead of being plated with the halide.

Preliminary cells showed that it was necessary to remove oxygen completely from the silver electrode. This was done, following Güntelberg,[15] by bubbling pure nitrogen through the cell electrolyte for three or four hours. The tube containing the silver electrode was broken under acid previously freed from oxygen. Electrical equilibrium in the cells was quickly reached after saturation with hydrogen. Usually, however, the cells were placed in the thermostat at night and the readings taken the next morning. Each cell contained two hydrogen electrodes and these usually agreed to 0.02 or 0.03 millivolt. The ther-

[13] Lewis, Brighton and Sebastian, J. Am. Chem. Soc. **39**, 2245 (1917).

[14] Randall and Young, J. Am. Chem. Soc. **50**, 989 (1928).

[15] Güntelberg, Zeits. f. physik. Chemie **123**, 199 (1926).

TABLE I. *Electromotive force of cells.*

Cell No.	Solid phase	Molality HCl	Molality HBr	Barometric pressure	Observed e.m.f.	Standard e.m.f.
1	solid sol.	0.5087	0.002677	754.0	0.2465	0.1018
2	solid sol.*	.5096	.002684	754.0	.2479	.1034
3	solid sol.*	.5093	.002681	756.0	.2466	.1020
4	solid sol.	.5088	.002679	756.0	.2476	.1029
5	solid sol.	.09994	.0005260	754.7	.3283	.1015
6	solid sol.	.09941	.0005232	754.7	.3284	.1014
7	AgCl	.5094	——	757.5	.2709	.2228
8	AgCl*	.5094	——	757.5	.2709	.2228
9	AgCl	.1151	——	748.6	.3450	.2228
10	AgCl	.1151	——	752.7	.3454	.2231
11	AgBr	——	0.5224	756.9	.1161	.0714
12	AgBr	——	.5229	756.9	.1162	.0715
13	AgBr	——	.1236	750.6	.1904	.0725
14	AgBr	——	.1240	750.6	.1900	.0722

* Material from calorimeter after specific heat runs.

mostat contained oil and was held at 25°C ±0.02°. The electrical system was the same as that used by Lewis, Brighton and Sebastian[13] except for the substitution of a Leeds and Northrup Type K potentiometer instead of the volt box. The concentration of acid used was determined after completion of the measurements, samples being taken from each side of the cell.

The experimental observations are recorded in Table I. In this table, the first column designates the cells by number. In column 2 are indicated the solid phases, prepared as described above, employed in the silver electrode. The molalities (moles per 1000 g H_2O) of the acids in the cell electrolytes, determined by analyses of samples drawn from each side of the cell, are given in columns 3 and 4. The barometric pressure in mm is shown in the fifth column. The observed electromotive forces in volts, recorded in column 6, are averages of readings taken over a period of several days after the cells had reached equilibrium, i.e., after variations were reduced to less than 0.2 mv. The cells generally became steady in about four hours, and were consistent and reproducible, within the limits required in this work.

For the comparison of the individual cells, and in the calculations of free energy, it is convenient to have the standard electromotive forces, $E°$. The values obtained for $E°$ for each cell are listed in the last column of Table I. The formula employed in the calculations is

$$E = E° - 0.05915\ (A \log a_{HBr} + B \log a_{HCl} - \tfrac{1}{2} \log p_{H_2}).$$

In this equation, E and $E°$ are, respectively, the observed and standard electromotive forces. The activity of the acids is represented by the symbol a with the appropriate subscript, and the partial pressure of hydrogen by p_{H_2}. The factors A and B represent the mole fraction of silver bromide and silver chloride, respectively, in the solid solution. The required activity values are obtainable from the determinations of activity coefficients by Scatchard[16] for HCl and of Livingston[17] for HBr, with the assistance of the principle of ionic strength[18] in the case of the mixed electrolytes.

The average value of $E°$ for the cells involving the solid solution, for which the individual values are given in Table I, is 0.1022 volt. For the cells containing pure silver chloride it is 0.2229 volt, and for the silver bromide cells 0.0719 volt. From these, the e.m.f. corresponding to the formation of one mole of our solid solution from 0.728 mole

[16] Scatchard, J. Am. Chem. Soc. **47**, 641 (1925).

[17] Livingston, J. Am. Chem. Soc. **48**, 45 (1926). As far as we have been able to ascertain, Livingston did not exclude oxygen from the electrolytes in his cells. This may have influenced his activity coefficients to some extent. We believe the uncertainty in these values to be in part responsible for the relatively large difference in $E°$ for the silver bromide cells with 0.5 M and 0.1 M HBr. These inaccuracies are, however, not serious in the present connection.

[18] Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., New York, 1924.

TABLE II. *Heats of solution of AgBr, AgCl, and the solid solution in a thiosulfate solution at 25°.*

Substance	Moles of substance used	Temperature rise of calorimeter, °C	Heat capacity of calorimeter, cal.	Heat of solution, cal./mole.
AgBr	0.05928	0.02607	1227.7 1230.6	
			Av. 1229.1	540.5
	0.05932	0.02589	1223.2 1224.5	
			Av. 1223.8	534.2
				Av. 537.4
AgCl	0.05929	0.2470	1227.5 1229.2	
			Av. 1228.4	5118
	0.05929	0.2484	1223.0 1221.3	
			Av. 1222.2	5120
				Av. 5119
Solid Solution	0.05931	0.09000	1226.6 1229.8	
$AgBr_{0.728}Cl_{0.272}$			Av. 1228.2	1863.7
	0.05931	0.09004	1228.5 1228.4	
			Av. 1228.4	1864.8
				Av. 1864.3
Mechanical Mixture 0.04311 AgBr + 0.01623 AgCl	0.05934	0.08663	1224.9	1788.1 Calc. 1791.5*

* From values found for pure substances.

AgBr and 0.272 mole AgCl may readily be calculated. It proves to be $0.728\times0.0719+0.272\times0.2229-0.1022=0.0110$ volt. This corresponds to a free energy change for the reaction of 254 cal. The uncertainty in this value we think is not greater than 1 millivolt, or about 20 cal.

THE HEAT OF FORMATION OF THE SOLID SOLUTION

The heat of formation of our solid solution was determined by measuring the heat effects when the mixed crystals and each of the pure constituents were dissolved in separate portions of a thiosulfate solution.

The apparatus and procedure used were those described by Randall and Rossini.[19] The sodium thiosulfate solution, identical in each of the runs, was made up in the proportion of 1100 grams of water to 200 grams of recrystallized (and partially dehydrated) sodium thiosulfate, which were also the amounts used in the calorimeter. After each determination of a heat of solution, the heat capacity of the calorimeter and its contents was twice determined. Measurements were made on two samples each of the solid solution and the

[19] Randall and Rossini, J. Am. Chem. Soc. **51**, 323 (1929). We express our thanks to Dr. Rossini for valued assistance in these measurements.

pure constituents, and on one sample of a mechanical mixture made up approximately in the proportion of the solid solution. The results are summarized in Table II, which is self-explanatory.

From these results it is found that the change in heat content in the formation of one mole of the solid solution is 80.7 cal. at 25°. This value we consider to be correct to ±10 cal.

Heat Capacity and Entropy of Silver Bromide and Silver Chloride and The Solid Solution

This portion of the experimental work consisted in the determination of the heat capacities of the two pure constituents and the solid solution between 298° and 15°K.[20] The apparatus used and procedure followed in the specific heat runs were, with minor exceptions, the same in type as generally employed in low temperature work in this laboratory at the time of these measurements (1928). The technique is so much standardized that detailed description is not required here.[21] The amounts of the materials used in the measurements of heat capacity were as follows: 122.28 g = 0.6511 mole AgBr; 121.01 g = 0.8442 mole AgCl; 104.22 g = 0.5931 mole solid solution (weights corrected to vacuum). We show in Table III the results of the measurements. The temperatures and corresponding molal heat capacities there shown are means over intervals ranging from 2 to 5°.

From these data the entropy difference $S_{298}-S_0$ of each substance was obtained graphically on large scale plots of C_p against log T. The necessary extrapolation to the absolute zero from the lowest temperatures of measurement was made with the assistance of Debye and Einstein functions combined in such a way as to fit the experimental points (within 0.08 cal.) up to 50°K. Entropies at the lowest measured point were then obtained from calculated values for these functions. The entropy terms resulting from these extrapolations amounted to 0.90, 0.43 and 0.50 cal./mol/deg. for the silver bromide, the silver chloride and the solid solution, respectively. The difference $S_{298}-S_0$ was found to be 25.62 for silver bromide, 22.97 for silver chloride, and 24.99 for the solid solution.

We estimate that the uncertainty in the values of these entropy differences is less than 0.1 cal./mol/deg., and consider that the differences among these quantities themselves are not less accurate than this because of the nearly identical treatment given each substance.

It is to be noted that $S_{298}-S_0$ for the solid solution as determined directly above does not differ significantly from that of a mechanical mixture of the same proportions. The value for the solid solution is 24.99, while that calculated for a mechanical mixture is 24.90.

It is also important to note the detailed behavior of the specific heats with respect to the additive law. For this purpose Table IV, showing values of ΔC_p in the formation of a mole of the solution from its constituents, as obtained by combining values from the smoothed curves at equal intervals in log T, has been constructed.

It will be seen that the difference between the observed value of C_p for the solution from that of the components in the pure state is less than 0.1 percent in the higher temperature range, and therefore well within the experimental error. At the lowest temperatures of our measurements, however, the difference has increased, but is still less than 1 percent. This difference is slightly greater than we should attribute to experimental uncertainty, yet not enough to permit us to say that there are significant departures from the additive law. If any such departures occur they do so at temperatures outside the range of our measurements.

Collected Results

The reaction that we have studied may be written,

$$0.728\ \mathrm{AgBr(cryst.)} + 0.272\ \mathrm{AgCl(cryst.)} = 0.728\ \mathrm{AgBr}\cdot 0.272\ \mathrm{AgCl(cryst.\ solution)}.$$

[20] Since the completion of our specific heat work, other measurements for AgCl and AgBr have been published. Clusius and Harteck, Zeits. f. physik. Chemie **A134**, 243 (1928), studied AgCl from 10.5 to 126°K, and Eucken, Clusius and Wortinek (Zeits. anorg. Chem. **203**, 39 (1931)) AgBr between 11.8 and 273°K. These data are in general in good agreement with ours.

[21] Our apparatus was designed following suggestions of Professor W. F. Giauque, whose cooperation in the specific heat measurements is much appreciated. A set-up similar in most essentials to ours is described by Latimer and Greensfelder, J. Am. Chem. Soc. **50**, 2202 (1928).

TABLE III. *Molal heat capacities of silver bromide, silver chloride, and the solid solution.*

AgBr		AgCl		Solid Solution	
T	C_p, cal./mole	T	C_p, cal./mole	T	C_p, cal./mole
24.04	3.520	15.00	1.122	16.04	1.643
28.31	4.516	18.09	1.767	19.94	2.468
32.81	5.417	21.07	2.259	24.32	3.385
37.43	6.226	24.71	2.878	29.26	4.469
41.69	7.086	28.70	3.623	34.62	5.468
45.87	7.562	32.60	4.273	39.68	6.240
50.54	8.006	37.37	4.941	44.22	6.933
55.28	8.508	43.04	5.735	48.37	7.418
60.19	8.924	48.33	6.405	52.51	7.883
69.34	9.689	53.65	6.926	56.68	8.334
74.42	9.972	58.32	7.390	60.46	8.635
83.65	10.305	62.42	7.788	64.39	9.027
93.09	10.658	75.17	8.779	68.25	9.293
101.56	10.982	79.39	9.019	73.35	9.600
108.35	11.164	88.56	9.501	76.99	9.780
115.49	11.293	97.29	9.865	80.92	9.959
124.17	11.439	105.91	10.230	85.12	10.106
134.97	11.497	114.16	10.493	89.09	10.276
142.72	11.621	122.66	10.682	92.84	10.396
150.67	11.749	130.58	10.834	96.89	10.514
158.16	11.810	138.45	10.988	101.16	10.682
166.78	11.945	140.65	11.021	105.22	10.807
175.62	11.964	149.13	11.203	110.64	10.984
183.93	12.088	157.90	11.401	114.65	11.080
192.05	12.240	166.07	11.548	119.05	11.109
200.34	12.155	174.28	11.582	123.31	11.201
212.26	12.332	183.13	11.640	127.50	11.223
222.71	12.297	191.01	11.760	135.85	11.353
235.33	12.222	200.24	11.876	143.02	11.471
246.17	12.326	209.80	11.993	144.83	11.544
258.95	12.300	210.54	12.030	152.53	11.658
269.70	12.406	220.82	12.048	160.55	11.608
279.24	12.452	230.73	12.083	168.72	11.825
289.29	12.375	240.40	12.061	176.80	11.861
		250.36	12.182	184.09	12.090
		260.54	12.137	191.64	11.945
		270.43	12.050	198.78	12.100
		284.97	12.135	206.36	12.140
		292.12	12.080	215.08	12.230
				231.99	12.228
				239.96	12.193
				247.81	12.189
				251.99	12.225
				261.20	12.302
				274.39	12.275
				287.13	12.228
				293.45	12.196

TABLE IV. *ΔC_p in the formation of the solid solution from the pure constituents.*

log T	1.25	1.50	1.75	2.00	2.25
C_p solid solution	2.000	4.945	8.295	10.660	11.920
C_p pure constituents	1.982	4.899	8.240	10.679	11.921
ΔC_p	0.018	0.046	0.055	−0.019	−0.001

We have determined by standard methods of thermodynamics the values of ΔF and ΔH for this reaction at 298.1°K. The well-known relation, $\Delta S=(\Delta H-\Delta F)/T$, between these quantities and the entropy change permits the calculation of the latter. We have thus found;

$$\Delta F_{298}=-254\pm20 \text{ cal.};$$

$$\Delta H_{298}=81\pm10 \text{ cal.};$$

$$\Delta S_{298}=1.12\pm0.10 \text{ cal./deg.}$$

From the specific heat measurements we have obtained the change in heat capacity for this

reaction in the temperature interval 15−298°K. At no point within this range was the change in heat capacity significantly different from zero. That is

$$\Delta C_{p\ 15-298}=0.$$

Making the assumption that this relation will remain true at all temperatures down to absolute zero, it follows that ΔS at the absolute zero is not zero, but is the same, within experimental error, as at 298°K, or about 1.1 e.u.

Stated in another way, we have found from the specific heat curves, with the assumption of zero entropy for each substance at the absolute zero, that for

$$\text{AgBr},\quad S_{298}=25.62\pm0.1\ \text{cal./deg.},$$

$$\text{AgCl},\quad S_{298}=22.97\pm0.1\ \text{cal./deg.},$$

$$\text{Solid solution},\quad S_{298}=24.99\pm0.1\ \text{cal./deg.}$$

From which we find, allowing about the same accuracy for the entropy difference as for the "absolute" values,

$$\Delta S_{298}=0.09\pm0.10\ \text{cal./deg.}$$

This last result does not differ from zero by more than the possible experimental error, and is in conflict with the result found above by established methods. From this angle, therefore, the apparent result of our measurements is this: if the entropies of the pure salts at the absolute zero are taken as zero, the solid solution at this temperature must be assigned a value of about 1.1 units of entropy.

We believe these results to be typical and shall in the following section discuss their interpretation.

Interpretation of Results

The entropy change at the absolute zero obtained above depends in part upon an extrapolation of the specific heat measurements. It is possible to claim, therefore, that departure from the accepted curves may occur at very low temperatures in such a way as to make $\Delta S_0=0$. The systems we have studied seem to us very unlikely to exhibit specific heats near the absolute zero that would not be predictable from the experimental curves at higher temperatures. It appears still less likely that any abnormalities that may exist at very low temperatures will make the additive law ($\Delta C_p=0$) untrue. We consider, therefore, that objections to the experiments from this standpoint are invalid in the present case.

A further objection that has been strongly urged[22] against experiments of this type arises from the fact that in the lower temperature range the solid solution becomes thermodynamically unstable, and, if equilibrium were maintained, would separate into two phases. With approach to the absolute zero these would approach the pure salts in composition. Even at temperatures where no separation of phases tends to occur, the establishment of the ultimately stable condition may be a very slow process. Long annealing may be expected to produce phases differing in properties from those not allowed to come to equilibrium, and the heat capacities of the latter will depend upon their age at the time of measurement. The argument then is that no ideally reversible isothermal process, and no reversible heating or cooling, involving a phase slowly shifting through a series of unstable states is possible. Since reversible processes are essential to the measurement of entropy differences, unstable "frozen" phases must be excluded from thermodynamic consideration. From this standpoint, it is meaningless to speak of the entropy difference between the solid solution and the pure substances at the same (low) temperature, since none can be ideally determined.

The practical difficulty attending a reversible isothermal process involving a frozen phase must be at once admitted. It is also true that the ordinary process of reversible heating to a temperature permitting the isothermal change, followed by reversible cooling of the products to the original temperature, cannot be carried out in the strictly idealized fashion. In real processes of this kind, however, very close approach to reversibility, in the sense that the total entropy change of system and surroundings is insignificantly small, can be attained. In such processes the materials may be transferred successively between a series of heat reservoirs differing from each other in temperature by a small, but finite, amount, remaining in each for a finite time long enough for close approach to temperature equalization but

[22] See for example the able review by Simon, Ergebnisse d. exakten Wissenschaften 9, 222 (1930).

not for equilibrium of any other sort. Such a process is essentially reversible; as much so, for example, as many "reversible" galvanic cells operating with finite currents. Moreover, failure of complete reversibility does not invalidate the calculation of entropy changes. It merely limits the exactness of the result.[23] The inaccuracy in many cases may be made very small in the real process. Moreover, by appropriate extrapolation of results to zero times (of contact) and zero temperature differences between reservoirs in suitably conceived real processes, the result of an ideal process of the same sort could no doubt be obtained with high accuracy. As the strictly reversible process is an idealized one in any event, it is perhaps simpler to invoke the aid of ideal catalysts, infinitely accelerating the desired processes, or excluding the undesired. The difficulties attending realization of ideal reversibility then vanish. These difficulties, regardless of what method may be chosen for overcoming them, are connected solely with rate effects and are extraneous to thermodynamics. In the light of these considerations we see little force to the objections discussed above, and claim that the calculation of $(S_T - S_0)$ as $\int_0^T C_p d \ln T$ for frozen phases is amply justified.

Quite different and perhaps more subtle questions arise when the problem is viewed statistically. As is well known,[24] the concepts of statistical mechanics and thermodynamics can, in general, be brought into correct relationship by the assumption that the entropy of a system[25] in a given state is $S = k \ln Z$. In this equation Z is the number of distinguishable configurations or detailed states comprising the macroscopic state in question. Adopting this view, the entropy change in the formation of our crystalline solution can be calculated. Effects resulting from mixing of isotopes, and nuclear spin effects, are without interest in the present connection and may be ignored. In the pure substances, then, only one distinguishable state, in the sense first used by Bose and Einstein, appears to be possible at the absolute zero. In the solid solution, however, each interchange of a bromide with a chloride ion gives rise to a new state. The number of physically different possible exemplars of the solution is therefore the number of distributions of the two unlike negative ions over the corresponding positions in the lattice. It may be shown[4] to be $N!/(X_1N)!(X_2N)!$. This is the factor by which Z for the solid solution exceeds Z for the pure substances. In it, N is Avogadro's number, and X_1 and X_2 are the mole fractions of the constituents. The usual application of Stirling's approximation leads to the relation,

$$\Delta S = -RX_1 \ln X_1 - RX_2 \ln X_2.$$

This equation is identical with that obtained thermodynamically for perfect solutions, and is closely substantiated by the measurements above, which yielded 1.12 ± 0.1 for the entropy of mixing, as compared with 1.16 calculated by the formula. The solution, of course, is not perfect since its molal heat content and free energy differ by 80 calories from the ideal values. It is of much interest to find that the equation of entropy of perfect solutions may nevertheless be applied. We believe the statistical and experimental verification of this point in the present example justify its acceptance in all similar cases, irrespective of the degree of perfection of the solution as judged by other standards.

The experimental measurements at 298°K were made under conditions permitting an interchange of the atoms of the solid solution upon the crystal lattice. Under such circumstances there can be little question that the number of states in the solid solution is greater than in the pure substances by the factor obtained above. Under other conditions, however, an apparent difficulty arises.

Thus, as the temperature is lowered during the specific heat measurements the interchange of

[23] A small error is of course unavoidably introduced in calculations like ours. This arises from the fact that some part of the unstable material must undergo a change during the measurement of heat capacities in certain temperature ranges. The measured values therefore do not all correspond to absolutely identical phases. This error we consider trivial in the present instance. It is similar in type to that in the analogous cases of monoclinic sulfur or finely divided white tin below their transition points, and perhaps not so difficult to eliminate.

[24] Cf. Lewis and Mayer, Proc. Nat. Acad. Sci. **14**, 569 (1928).

[25] The controversy concerning the merits of absolute as opposed to relative entropy is of no interest here. In our opinion it involves only questions of convenience and taste. We have used throughout either language without distinction.

atoms is effectively prohibited. Throughout these measurements, and at the absolute zero, a single configuration of the crystalline solution is represented. Its entropy, therefore, in quantum statistics as ordinarily applied, apparently should be taken as zero at the absolute zero. If it is so taken, some portion of the thermodynamic argument is invalidated. It is obviously necessary, therefore, to modify the thermodynamic or the statistical interpretation.

If the first course is chosen, the point of attack is again sought in the change from the condition of complete equilibrium in the e.m.f. measurements to the "frozen" system in the specific heat work. It may be claimed that the reduction from $N!/(X_1N)!(X_2N)!$ to one in the number of configurations accessible to the solid solution represents a change in thermodynamic as well as statistical constraints, equivalent to a complete change in the nature of the system. Correspondingly and automatically, the entropy of the solid solution in the constrained state should be reduced relative to that of the unconstrained system by the amount of the entropy of mixing. This term should then be included in the entropy of the solid solution or not, depending upon the ability or inability of the atoms (or molecules) to make frequent interchanges in times comparable to the duration of the phase in the intended application. In other words, allowing time for interchange introduces, and "freezing" excludes, an irreversible process, in which, effectively, a pure "compound" is converted into a solution of the same composition, and which is accompanied by the entropy increase $-\Sigma RX \ln X$.

This position, however, is tenable only if the validity of thermodynamics applied to phases of this type is denied. Otherwise, no latitude in the assignment of entropy is possible, no irreversible process may be assumed in the passage between the frozen and the unconstrained system. For, as previously outlined, a cycle involving these states can be completed without significant increase in entropy of the surroundings. A change of entropy of the kind claimed is therefore not demonstrable. As we see it, the constraints operative in the frozen system act solely to maintain the unstable systems in preference to the stable. They introduce no ambiguity in the entropy of the phase as it actually occurs. To reject this conclusion would seriously damage the structure of thermodynamics. The severe and unnecessary limitations that would be imposed by such a course could be compensated only through detailed knowledge respecting the presence and nature of frozen equilibria in all systems treated by either the third or the second law. We think, therefore, that the conflict in ideas is best resolved by modifying the statistical interpretation.

Such a modification has been proposed by Lewis.[26] According to him, Z in the equation defining entropy represents the total number of states which, so far as the observers information extends, are possible configurations of the system. The ease or speed with which the system may pass from one to another of the permitted configurations is in this view unimportant. Thus, in the present case, when the atoms of the crystalline solution become frozen in fixed positions the particular pattern is unknown. The number of configurations in doubt (not excluded by information possessed by the observer) is as great as if free interchange of the atoms on the lattice were occurring. At the absolute zero this situation still obtains. To the solution, therefore, is to be assigned positive entropy, in amount calculated above, representing the observers lack of information. For any *specified* configuration of the solution, the entropy again becomes zero.

The statement of the situation most acceptable to us may be outlined somewhat as follows. The entropy change of a system is thermodynamically determined by the definition of the initial and final states. In considering a particular entropy change statistically, the definitions of the states of the system must be made to conform to the thermodynamic ones. In the crystalline solution near the absolute zero the state as ordinarily defined is not restricted to a single detailed pattern. It is indefinite in the sense that it may consist of any one of a large number of detailed states, lying within a band of energies, each of which states falls within the thermodynamic definition, and might be regarded as an exemplar of the system. This indefiniteness, which is imposed by the nonselective character of the process of formation, must be embodied in the statistical definition by taking Z as equal to the number of different permitted exemplars. If a process could be invented

[26] Lewis, Science **71**, 569 (1930).

by which some one configuration could be reversibly obtained at will to the exclusion of all others, the definition of the state would be correspondingly narrowed, and the entropy would be zero. In the absence of ability of the observer thus to work with a single detailed state, multiplicity must be admitted in fixing Z. This position seems to us to meet adequately the present requirements, without undue strain in the accepted ideas of statistics.

The distinction between the opposed viewpoints sketched above impresses us as in no sense trivial. Practically, perhaps, it is unimportant, since the advocates of either argument will in general achieve correct results in applications. In its larger aspects the controversy, which is still an active one, involves rather fundamental ideas. On this account we have given in detail, at the risk of obviousness, the reasons supporting the retention of the thermodynamic conclusion as to the finite entropy at 0°K of the solution, and the interpretation of statistical ideas to agree with it.

We wish to make it clear, however, that the arguments advanced here are not directed against the existence of a generally valid thermodynamic and statistical theorem relating to entropy at the absolute zero. We cannot, therefore, endorse the "ruthless" attitude adopted by Fowler and Sterne.[27] These authors would abandon the third law because entropy changes in real systems do not always become zero with approach to the absolute zero, and because it is not always easy in practice to tell when they do. It has, of course, become increasingly clear in recent years that blind application of the law, even to "pure" crystals, must often result badly. The various cases discovered and explained by Giauque and his coworkers,[28] and the statistical work of Fowler and Sterne, are conclusive on this point. Nevertheless, a substantial number of systems of diverse types[22] may be handled in the ordinary way. The exceptional cases deviate through a uniform cause discussed below. Already much progress has been made toward the prediction of the occurrence and extent of deviations. There is every reason to expect that such predictions will in the future be pretty generally possible. The doubt expressed by Fowler and Sterne regarding the utility of the third law is, we should state, the only feature of their work bearing on the present question to which we cannot subscribe. We should mention particularly that their device in the treatment of the entropy of mixing in frozen phases leads to the inclusion of the mixing term as part of the entropy, as we have claimed here.

Although the fundamental basis and the limitations of the third law are very generally understood, a concise formulation of it proves a little elusive. The statements in most general use associate zero entropy with the perfect crystalline[29] (perfectly ordered) condition, or with the condition of lowest energy (lowest quantum state),[30] usually assumed to be "ordered" also. The attempt to define a "perfect crystal" encounters various difficulties not originally contemplated, such as the possibility of mosaic crystals, which are not perfect in the ordinary sense, but must be included in the law. More serious is the frequent occurrence of crystalline solutions of various types (including random distributions on the lattice of isotopic atoms, random orientations of nuclear spins, etc.), which may be quite perfect crystallographically, but do not conform to the law. These difficulties may be met by resorting to the requirement of perfect order. We believe, however, that while the condition of complete order is a sufficient criterion, it is not a necessary one. We see no necessity or support, for example, for the assumption of perfect order of the molecules of degenerate gases, or of the electrons in metals (if they obey Fermi statistics) at the absolute zero, although the entropy of such phases apparently must be taken as zero. Even the atoms of a perfect crystal are, according to the ideas of quantum mechanics, in vibratory motion at the absolute zero. This, and also the uncertainty principle, clouds the concept of perfect order of the atoms but is without necessary effect upon the entropy. The criteria of lowest energy and lowest quantum state avoid any necessary

[27] Fowler and Sterne, Rev. Mod. Phys. **4**, 635 (1932).

[28] See for example (a) Giauque and Johnston, J. Am. Chem. Soc. **50**, 3221 (1929); (b) Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929); (c) Giauque, J. Am. Chem. Soc. **52**, 4816 (1930); (d) Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932); (e) Giauque and Ashley, Phys. Rev. **43**, 81 (1933).

[29] Lewis and Randall, reference 18, 444–448.

[30] Simon, reference 22, 231, and other authors there cited.

implication of order, but are themselves either unnecessary or insufficient. Thus, unstable crystals, like diamond, are of zero entropy but not lowest energy,[31] and the atoms of crystalline solutions are presumably all in their lowest vibrational levels, though the entropy cannot be taken as zero.

The goal in the search for an adequate formulation is, of course, to find some property, preferably a thermodynamic one, which can be rigidly correlated with statistical singleness of state, and therefore with zero entropy. The conspicuous examples of substances that do not have zero entropy at the absolute zero are glasses and solutions. These differ significantly from other phases at the absolute zero only in the fact that the exemplars of a given system differ among themselves, and comprise a large group of distinguishable states. We believe that these states cover a "band" of energies, which may often be very narrow but never absolutely sharp. We suggest, therefore, as a simple, comprehensive, and sufficiently restrictive statement of the third law that *the entropy of any phase of sharply specifiable energy is zero at the absolute zero.* All systems in states of lowest energy or perfect order conform to the limitation in this statement, which thus includes the formulations based on these criteria. In addition, certain other phases unnecessarily excluded by the other statements are included by the preceding one, which seems to us therefore more appropriate.

The reason for ascribing a characteristic energy to each isomer of a crystal of a solid solution lies in the assumption that the interaction of the molecules differs to a significant, though very small, extent among the different arrangements, however close the similarity of the individual molecules may be. In the absence of exact specification of energy (exact within the meaning of the uncertainty principle), limiting the system to some one of the possible arrangements, a multiplicity, and therefore a finite entropy, for the loosely defined macrostate ensues. In many cases, of course, entropy changes in ordinary reactions involving such states (for example, mixtures of isotopes) will be zero, making it possible to take the "practical" entropy as zero at 0°K, for these phases.

Every known deviation from zero entropy by "pure" crystalline phases at 0°K may be connected with a random distribution of two or more distinguishable types of molecules or atoms over the crystal lattice. In illustration, we would recall that even a difference in orientation may distinguish otherwise similar molecules in a lattice, as proposed by Clayton and Giauque[28d] to explain the entropy, $\frac{1}{2} R \ln 2$, of their crystals of carbon monoxide at the absolute zero. As a further example, we cite "ordinary" crystalline hydrogen, which we define as a solution of para-hydrogen molecules, of fixed mole fraction equal to $\frac{1}{4}$, with nine kinds of ortho-hydrogen molecules, whose individual mole fractions may vary between $\frac{3}{4}$ and 0. The enumeration of the accessible states for this phase gives

$$Z = 9^{3N/4} N!/(N/4)!(3N/4)!,$$

as found by Fowler and Sterne.[27] The entropy then proves to be[32] $R(\frac{3}{4} \ln 3 + \ln 4)$, in agreement

[31] The attempt to rescue the lowest energy formulation (compare Simon, reference 22, 231) by invoking as an additional criterion the presence of potential crests between crystal forms of different stability is unsatisfactory because such crests exist between the exemplars of all glasses, or glassy or crystalline solutions. It is worth while, we think, to emphasize the close analogy between various exemplars of an unstable crystalline solution and a series of different forms of unstable pure crystals of a single substance. In each there is a potential crest separating the various possible states. Every atom in either type of crystal is presumably in a position of minimum energy. Exchanges in position of atoms on the lattice of the crystalline solution, which result in the production of stabler "isomers," require an activation energy comparable in type and magnitude with the similar quantity in transitions between the forms of the pure crystals. The energy difference between the forms of highest and lowest energy is also comparable in magnitude in the two sets. The crystalline solutions of ordinary type differ from pure crystals primarily in the greater number of forms or isomers intermediate between those of highest and of lowest energy, and the consequent smaller difference in total energy between successive forms.

[32] It is interesting to note that without the specification of a fixed mole fraction for the para form, it would be necessary to assume $Z = 10^N$ and $S_0 = R \ln 10$. There is perhaps some question as to whether ordinary gaseous hydrogen might not be defined in such a way as to require this value of S_0 for the "frozen" crystal at 0°K. We consider it legitimate, however, if not indeed necessary to include a specification of the energy of the sample which would narrow the proportion of ortho to para practically to 3 to 1.

with Giauque's result.[28c] These substances and the other "irregular" ones are therefore actually crystalline solutions. The results obtained by direct measurement in the very simple system we have studied seem to us to offer important confirmation of the treatment which has been given these less obvious cases, which cannot be so directly studied.

The limitations we have discussed above apply with equal force to the "principle of the unattainability of the absolute zero," which is often allied or identified with the third law. This principle, insofar as it is regarded as a thermodynamic law, is violated by the recognition of entropy changes that remain finite as the absolute zero is approached. In its unrestricted form, it may very well be universally true, for reasons connected with rate effects. In this form, however, some of its thermodynamic conclusions are incorrect. In limited form it adds nothing to the third law. It therefore seems to us advisable to eliminate it from the list of thermodynamic tenets.

The Mechanism of the Reaction of Hydrogen Atoms with Oxygen

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(1) A mechanism has been suggested for the reaction of hydrogen atoms with oxygen. This mechanism unifies a considerable number of hitherto conflicting data which have been assembled in connection with studies of the reaction. (2) The rate variation with the concentration of hydrogen and oxygen has been explained. (3) The quantum yield has been predicted, using the same constants as those necessary to reproduce the rate variation. Also the variation of quantum yield with light intensity is found to be as predicted. (4) The temperature coefficient is also as predicted by the mechanism, but agreement is only semi-quantitative. (5) The bearing of this mechanism on a series of reactions which have been and are still under investigation has been indicated.

IN a number of recent investigations[1] it has been shown that many of the current ideas of the mechanism of the reaction of hydrogen atoms with oxygen must be revised. In particular it was demonstrated that experimental results did not at all agree with the mechanism suggested by Haber and Bonhoeffer[2] and revised by Frankenburger and Klinkhardt.[3] Several mechanisms were suggested which, it was thought, agreed better with the sum total of the available experimental data. At that time, however, no attempt was made to obtain a quantitative proof of the exactness of any of the reactions schemes postulated. It is the purpose of this work to propose a mechanism which agrees with a remarkable degree of exactitude with all the measurements which have been carried out on the reaction.

EXPERIMENTAL DATA

Products of the reaction

It has been quite conclusively demonstrated by Salley and Bates that hydrogen peroxide constitutes at least 85–90 percent of the primary products of the reaction of dry gases. This has been indicated also in the work of Marshall[4] and of Bonhoeffer[5] and Boehm for moist gases. Salley and Bates were of the opinion that hydrogen peroxide was the sole product, the 10–15 percent water being the result of decomposition of the peroxide.

Yield of peroxide per hydrogen atom (quantum yield)

Measurements of Marshall[6] show 2.5 molecules of hydrogen peroxide per absorbed quantum for electrolytic gas. Later measurements of Frankenburger and Klinkhardt[3] gave a mean value of 1.2 for a gas containing but 2–3 percent oxygen.

Effect of concentration on the mercury sensitized reaction

Measurements of Marshall indicate that at 60°C the rate of this reaction is proportional to the mole fraction of hydrogen present:

$$d[H_2O_2]/dt = K \quad [H_2]/[H_2]+[O_2].$$

This would seem to show that hydrogen and oxygen are equally efficient in receiving the energy of an excited mercury atom on collision. However, the measurements of Zemansky[7] on relative quenching efficiencies give values of $tk/p = 1.10$ for hydrogen and 0.68 for oxygen, where t is the lifetime of the mercury atom

[1] Salley and Taylor, J. Am. Chem. Soc. **55**, 96 (1933). Salley and Bates, ibid. **55**, 110 (1933). Lavin and Bates, ibid. **55**, 81 (1933). Bates, Proc. Nat. Acad. Sci. **19**, 81 (1933).

[2] Haber and Bonhoeffer, Zeits. f. physik. Chemie **A137**, 263 (1928).

[3] Frankenburger and Klinkhardt, Zeits. f. physik. Chemie **B15**, 421 (1932).

[4] Marshall, J. Am. Chem. Soc. **49**, 2763 (1927).

[5] Bonhoeffer and Boehm, Zeits. f. physik. Chemie **119**, 385 (1926).

[6] Marshall, J. Phys. Chem. **30**, 1078 (1926); J. Am. Chem. Soc. **54**, 4460 (1932).

[7] Zemansky, Phys. Rev. **36**, 919 (1930).

(1×10^{-7} sec.), p is the pressure of hydrogen or oxygen in mm of mercury, and k is the number of effective collisions for mercury atom per second. It can readily be seen that these give the bimolecular reaction constants for excited mercury and hydrogen and oxygen, k_{O_2} k_{H_2}, $=1.1$ and 0.68×10^7, respectively.[8]

Temperature coefficient of the reaction

Marshall's measurements of the temperature coefficient between 50 and 100°C give apparently discordant results. For example, he finds that with an arc current of 3 amperes he obtained 1.13 per 10°C, at 5 amp., 1.04, at 3 amp., 1.03. The more recent work of Salley and Taylor over a larger temperature range indicates that the temperature coefficient has a value of 1.07 between 400 and 490°C and a value of 1.39 between 510 and 530°C.

Light intensity. (Rate of formation of hydrogen atoms)

Marshall has shown that the rate of the reaction falls off from linearity at high arc currents, indicating that the rate is proportional to either the light intensity or to some fractional power of it, depending upon how this varies with the arc current.

Theoretical Considerations

Since most of the quantitative data available are connected with the mercury sensitized process, it is quite obvious that we must first concern ourselves with this reaction. It is generally conceded that this result of the collision of an excited mercury atom with a hydrogen molecule is two hydrogen atoms. Thus we may write:

$$Hg+h\nu\rightarrow Hg' \quad I_{abs.},$$

$$Hg'+H_2\rightarrow 2H+Hg \quad k_{H_2},$$

where $I_{abs.}$ represents the rate of absorption of light of wave-length 2537 by the mercury present in the system, or the rate of formation of excited mercury atoms. However, not all excited mercury atoms produce hydrogen atoms. Some are removed by collision with an oxygen molecule,

$$Hg'+O_2\rightarrow O_2'+Hg, \quad k_{O_2}.$$

This excited oxygen molecule is undoubtedly incapable of reacting with hydrogen molecules[9] and so any mercury atoms which transfer their energy to oxygen are "lost." Since, at the stationary state $d[Hg']/dt=-d[Hg']/dt$, it is evident that the rate of formation of hydrogen atoms will be given by the expression:

$$\frac{d[H]}{dt}=\frac{2[H_2]k_{H_2}I_{abs.}}{[H_2]k_{H_2}+[O_2]k_{O_2}}.$$

As has been stated, the values of k_{H_2} and k_{O_2} are known from quenching data, and this expression then reduces to

$$\frac{d[H]}{dt}=\frac{2.20[H_2]I_{abs.}}{1.10[H_2]+0.68[O_2]}.$$

The reaction of the hydrogen atoms with oxygen molecules, is generally conceded to be

$$H+O_2\rightarrow HO_2 \quad k_1. \qquad (1)$$

Previous to the work of Lavin and Bates[1] it was considered necessary that the molecule HO_2 so formed could only exist for an extremely short time without decomposing again to hydrogen atom and oxygen molecule, unless before this occurred the molecule suffered a collision in which it could give up its energy of formation. However, from the evidence offered by those authors it is quite plausible to write this expression in the form of a straight bimolecular reaction, at least at ordinary pressures.

The fate of the HO_2 molecule, however, has been the subject of considerable dispute. Taylor and Marshall have suggested

$$HO_2+H_2\rightarrow H_2O_2+H \quad k_{2a}, \qquad (2a)$$

$$H+H+M\rightarrow H_2+M' \quad k_{3a}. \qquad (3a)$$

As the concluding steps of the reaction, M represents the third body in the association of two hydrogen atoms. The rate of formation of hydrogen peroxide from these reactions can be shown to be

[8] These constants are expressed in mm reacting per mm of reactants.

[9] Kistiakowsky, J. Am. Chem. Soc. **52**, 1868 (1930).

$$d[H_2O_2]/dt=[O_2](k_1/k_{3a}^{\frac{1}{2}})([H_2]k_{H_2}I_{abs.}/([H_2]k_{H_2}+[O_2]k_{O_2})M)^{\frac{1}{2}}. \quad \text{I}$$

The mechanism suggested by Haber, and modified by Frankenburger and Klinkhardt, may be represented as substituting for reactions (2a) and (3a) the three alternative steps:

$$HO_2+H_2\rightarrow H_2O+OH\ k_{2b}, \qquad OH+OH\rightarrow H_2O_2\ k_{3b}, \qquad HO_2+H_2O\rightarrow H_2O_2+OH\ k_{4b}.$$

These lead to an expression for the rate of peroxide formation:

$$\frac{d[H_2O_2]}{dt}=\left[\frac{2k_{4b}[H_2O]}{[H_2O]k_{4b}+[H_2]k_{2b}}+1\right]\frac{k_{H_2}[H_2]I_{abs.}}{[H_2]k_{H_2}+[O_2]k_{O_2}}. \quad \text{II}$$

The reaction scheme which has been proposed by the present author[10] in a short note is

$$HO_2+H_2\rightarrow H_2O_2+H\ k_2, \quad (2) \qquad HO_2+HO_2\rightarrow H_2O_2+O_2\ k_3. \quad (3)$$

These two concluding steps lead to a rate expression:

$$\frac{d[H_2O_2]}{dt}=\frac{k_2}{k_3^{\frac{1}{2}}}[H_2]\left(\frac{[H_2]k_{H_2}I_{abs.}}{[H_2]k_{H_2}+[O_2]k_{O_2}}\right)^{\frac{1}{2}}+\frac{[H_2]k_{H_2}I_{abs.}}{[H_2]k_{H_2}+[O_2]k_{O_2}}. \quad \text{III}$$

In order to demonstrate the unique correctness of reaction III as compared with I and II, it is necessary to show that the former can be made to explain all the observed data, and at the same time to indicate that I, and II, will fall down in its relation to one or more of the parameters of the system.

Reaction I

Reaction I gives as the primary product of the reaction 100 percent hydrogen peroxide, in agreement with the experimental results. The quantum yield can vary between zero and infinity, depending upon the magnitudes of k_1 and k_{3a}, and thus, if a completely free adjustment of these can be made, the correct quantum yield can be obtained. The variation of rate with the square root of the light intensity might possibly also be in agreement with Marshall's results, since they did not exclude a square root relationship. The variation of the rate with $[H_2]$, $[O_2]$ is shown in column 6 of Table I, by giving the constancy of $k_1(I_{abs.}/k_{3a})^{\frac{1}{2}}$, which should remain constant over all variations of H_2 and O_2, if this be the correct mechanism. The value of M chosen is that of the total pressure ($[H_2]+[O_2]$). The experimental data are taken from Marshall. The value of R/N_{H_2} indicates the agreement of the empirical rate expression of Marshall, and is obtained by dividing the rate by the mole fraction of hydrogen. It can be readily seen that there exists no constancy in the value of $k_1(I_{abs.}/k_{3a})^{\frac{1}{2}}$ over the range of concentrations studied.

There might be some objection to the use of values of the total pressure for M in the rate expression I, since a collision of an O_2 molecule with two hydrogen atoms might result in the formation of a hydrogen peroxide molecule. However, it is quite easy to show that a substitution of the partial pressure of oxygen or of hydrogen for M, instead of the total pressure, does not make Eq. I fit the experimental results.

There is still another consideration which militates against the acceptance of I as the true mechanism. This is connected with the possible values of k_1 and k_{3a}. As we have already said, provided these may be chosen at liberty we can make this expression fit the quantum yield. However, we can show, from other considerations, that these constants must have values which would be in disagreement with the observed facts. Lavin and Bates have shown that k_1 must have such a value that only 1 in every thousand collisions is effective.

From this value and an approximate knowledge of the volumes of the apparatus used by Marshall, it is possible to obtain a value of the absolute magnitude of k_1 and k_{3a}. The total volume of Marshall's reaction system he estimates at 1500 cc (an explosion which destroyed his original

[10] Bates, J. Am. Chem. Soc. **55**, 426 (1933). Reaction (3) was also suggested by Salley and Bates.[1]

TABLE I.

Run No.	H_2 mm	O_2 mm	Rate $(-\Delta p)$ mm/min.	R/N_{H_2}	I		II			III			
					$\frac{k_1(I_{abs.})^{\frac{1}{2}}}{(k_{3a})^{\frac{1}{2}}}$	$I_{abs.}$	$3I_{abs.}$	$\left(\frac{k_2/k_3^{\frac{1}{2}}}{=1\times10^{-4}}\right)$ 1×10^{-3}	$\frac{I_{abs.}}{1.5\times10^{-3}}$	2×10^{-3}	10^{-2}	Mol/$h\nu$
1	364	475	0.92	2.14	0.075	5×10^{-13}	1.66	1.59	1.15	0.926	0.790	0.093	1.00
2	581	239	1.52	2.14	0.238	6×10^{-10}	1.91	1.83	1.19	0.953	.772	.083	1.60
3	775	58	2.00	2.15	0.878	9×10^{-9}	2.09	1.98	1.22	0.960	.736	.071	2.08
4	781	10	2.10	2.12	5.92	3×10^{-9}	2.11	2.00	1.22	0.962	.750	.066	2.18
5	146	699	3.0[a]	19.9	0.250		11.8		11.0	10.2			
6	425	368	12.3	21.2	1.16		20.4		16.8	15.8			0.78
7	740	20	20.	21.7	4.76		22.2		18.7	17.3			1.15
8	581	237	17–22[b]	24.7	2.48		24.4		21.2	19.9			

Runs 1–4, arc current 1 ampere; runs 5–8, 15 amperes.

[a] Value very uncertain. See Marshall, reference 4.

[b] Also apparently uncertain. Calculations based on average value (19.5).

The rates are all expressed in Marshall's unit, mm decrease in pressure per minute. Since he was removing his hydrogen peroxide as it was formed, these are in 0.5 mm of hydrogen peroxide per minute. It is especially to be observed that $I_{abs.}$ is expressed in the same units, which is equivalent to 0.5 mm of Hg′ being formed per minute. Since this is so, the quantum yield is obviously given by the ratio of $-\Delta p$ and $I_{abs.}$. The reaction constants are expressed then, in 0.5 mm reacting per mm of reactants, since they are all bimolecular.

set-up prevented an accurate volume measurement). The total volume illuminated he estimates at 220 cc. When 1500 cc of hydrogen peroxide at 0.5 mm and 20°C have been formed, $1500\times1.66\times10^{16}$ collisions have occurred, since there are 3.32×10^{16} atoms per cc at 1 mm and 20°C. The portion of the reaction system illuminated was maintained at 60°C in these experiments. The total number of collisions per minute in this volume at this temperature, and at a pressure of 1 mm can be calculated for any given molecular species by means of the kinetic theory. (See page 463.)

The value of a bimolecular constant expressed in the units of Marshall can be seen to be equal to the ratio of these two, provided every collision is effective. This comes out to be $\geqq10^8$. Since only 0.001 of the total collisions are effective $k_1=10^5$.

An evaluation of k_{3a} is a bit more involved. A three-body reaction can, in general, be divided into three distinct processes: the formation of the bimolecular association product, an energy rich quasi molecule, which then may either dissociate spontaneously, or be stabilized by collision with a third body. Formulating these three for the case in hand:

$$H+H\rightarrow H_2^*\ k_a, \qquad (1)$$

$$H_2^*+M\rightarrow H_2+M\ k_b, \qquad (2)$$

$$H_2^*\rightarrow H+H\ k_c. \qquad (3)$$

Here k_a and k_b are bimolecular reaction constants, and k_c is a unimolecular reaction constant and is equal to the reciprocal of the lifetime of the energy rich molecule. The two bimolecular constants will again be of the order of 10^8 or less, as already discussed in the case of k_1($k_a\leqq10^8$, $k_b\leqq10^8$). They will probably not differ from 10^8 by a very large amount. k_c we can show is of the order of magnitude of 10^{14}.[11] The rate of formation of hydrogen molecules will be governed by reaction (2), whence

$$\frac{d[H_2]}{dt}=[H_2^*][M]k_b$$

$$=\frac{[H]^2[M]k_bk_a}{(Mk_b+k_c)}=[H]^2M\ k_{3a}.$$

For ordinary pressures $M=10^2-10^3$, and Mk_b is equal to $10^{10}-10^{11}$ and may be nelgected as compared with $k_c=10^{14}$. It therefore follows immediately that

$$k_{3a}=k_bk_a/k_c=(10^8\times10^8)/10^{14}=100.$$

Substituting these values of k_1 and k_{3a} in $k_1(I_{abs.})^{\frac{1}{2}}/k_{3a}^{\frac{1}{2}}$ and solving for $I_{abs.}$ we obtain the values listed under column 6 of Table I. Since the quantum yield is given by the ratio of the rate divided by $I_{abs.}$, we can quite readily see that

[11] Steiner, Zeits. f. physik. Chemie **B15**, 249 (1932).

the mechanism of Taylor and Marshall would call for quantum yields which are many orders of magnitude greater than those experimentally determined. For these reasons, then, this mechanism cannot be accepted at the concentrations and light intensities employed. It is quite possible that at extremely low oxygen concentrations this mechanism might be involved, but not under those conditions under which our experimental data were obtained.

Reaction II

This reaction gives the quantum yield approximately as determined, and can be made to yield high concentrations of peroxide, provided k_{4b} is much greater than k_{2b}. In fact, Salley and Bates showed that, if this be the correct mechanism, $k_{4b}=5000\ k_{2b}$. (But these authors also failed to find the dependence on water concentration which this relationship would demand.)

In attempting to discover what agreement can be obtained for this rate expression, we must make use of the necessary assumption that $k_{4b}=5000\ k_{2b}$. Marshall's gases were always saturated with water vapor at room temperature, $H_2O=20$ mm. If we apply this fact to I it can be easily seen that $[H_2]k_{2b}/[H_2O]k_{4b}=700/100{,}000=0.007$ whence the expression H_2 k_{2b} may be neglected entirely and I simplifies to

$$\frac{d[H_2O_2]}{dt}=\frac{3k_{H_2}[H_2]I_{abs.}}{k_{H_2}[H_2]+k_{O_2}[O_2]}.$$

The constancy of 3 $I_{abs.}$ is shown by the values in column 7 of Table I. Again, there is not very good agreement. This fact, coupled with the reasons contained in the discussion of Salley and Bates, makes it appear necessary to discard this reaction scheme.

Reaction III

In fitting the experimental data to Reaction III it appears immediately that $k_2/k_3^{\frac{1}{2}}$ is an undetermined constant, whose value must be discovered in order to evaluate the constant, $I_{abs.}$, which is used to test the validity of the mechanism. The values of $I_{abs.}$ obtained from Marshall's data for values of $k_2/k_3^{\frac{1}{2}}$ from 10^{-2} to 10^{-4} are given in Table I, columns 9–13. In solving for $I_{abs.}$ two positive roots are obtained. One of these can be discarded, however, since to make this root fit Eq. III it would be necessary to take the negative value of the square root in III, which would have no physical significance under the postulates of the mechanism. If the various values of $I_{abs.}$ are plotted for each value of $k_2/k_3^{\frac{1}{2}}$ it can be seen that the four curves obtained for the cases where the arc current was one ampere, come very close to intersecting at a point where $k_2/k_3^{\frac{1}{2}}=1.5\times10^{-3}$. At points above and below this they become divergent. We shall accept then this value as the correct one for the reaction system of Marshall. This constant is thus chosen arbitrarily to give the best agreement among these four $I_{abs.}$ values in runs 1–4. Once chosen, however, it must remain constant for all data (within the experimental error) and must give good agreement with the other experimental facts connected with the reaction. It can be shown that the quantum yield, the effect on the reaction of a change in light intensity and temperature are all dependent upon the magnitude of this constant, $k_2/k_3^{\frac{1}{2}}$. Hence, if in choosing the value for it which fits the rate expression it appears that we have been given a freely adjustable constant, this is not so, since its value must also be governed by these other parameters. It will be shown that the value which gives a constancy for $I_{abs.}$ is also in agreement with the other facts connected with the reaction, and that furthermore, there is no known reason for ascribing to $k_2/k_3^{\frac{1}{2}}$ any other value.

When the values of $I_{abs.}$ for the reactions which were carried out at a higher light intensity are calculated the agreement is not as good as was the case in runs 1–4. However, runs 5 and 8 are distinctly uncertain and runs 6 and 7 differ by less than 10 percent. There is nothing in these data to indicate a lack of agreement with the theory.

The quantum yields for the various runs have been calculated for $k_2/k_3^{\frac{1}{2}}=1.5\times10^{-3}$ and are given in the last column of Table I.

As can be seen, these vary from unity to 2.18, depending upon the oxygen concentration employed. Such results are in complete agreement with the experimental determinations of this magnitude, which give values from unity to 2.5. The quantum yields will be dependent upon the light intensity, as well as the concentrations of H_2 and O_2, and the temperature, according to III. Thus, for example, in Fig. 1 is plotted the varia-

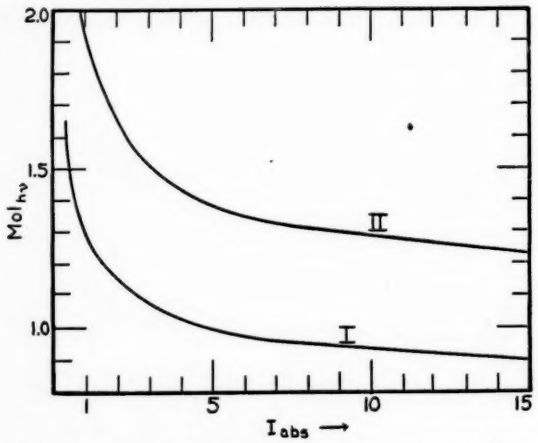

FIG. 1. Curve I: H_2, 400 mm; O_2, 200 mm; $k_2/(k_3)^{\frac{1}{2}}=1.5\times10^{-3}$. Curve II: H_2, 600 mm; O_2, 10 mm; $k_2/(k_3)^{\frac{1}{2}}=1.5\times10^{-3}$.

tion of quantum yield with light intensity. High ight intensities should give lower quantum yields than low intensities. In seeking to find experimental verification of this prediction of III it was found that Frankenburger and Klinkhardt used intensities a hundred-fold greater than did Marshall in his quantum yield determinations. Thus Frankenburger and Klinkhardt obtained rates of formation of hydrogen peroxide of 6 grams per hour, which is equivalent to $6.06\times(6/34)\times10^{23}=1.1\times10^{23}$ quanta per hour. Marshall employed 2.16×10^{19} quanta per minute, or 1.3×10^{21} quanta per hour. It can be seen at a glance that the data are qualitatively in agreement with the predictions, since Marshall reports a yield of 2.5 and the other authors a mean value of 1.2. The values of Frankenburger and Klinkhardt should be revised upward, since they found water in their products, which, according to the work of Bates and Salley, could only have come from a secondary peroxide decomposition. Assuming that $k_2/k_3^{\frac{1}{2}}=10^{-3}$ in both cases we may calculate approximate quantum yields as called for by III. By using the values $[O_2]=250$, $[H_2]=510$ for Marshall, and $[O_2]=20$ $[H_2]=740$ for the others. The light intensities must also be correlated as to order of magnitude with the $I_{abs.}$ of Table I if we are to use this value of $k_2/k_3^{\frac{1}{2}}$. The number of quanta per hour represented by $I_{abs.}=1$ is

$$\frac{6.06\times10^{23}\times1500\times60}{22400\times760\times2}=1.6\times10^{21}$$

quanta per hour, close to the intensity used by Marshall in his quantum yield measurements. Hence we shall take as the two light intensities $1.3/1.6=0.81$ and $110/1.6=69$. The quantum yields which result are 1.1 and 1.5 as compared with 1.2 and 2.5 reported. If the discrepancy were due entirely to water formed from secondary peroxide decomposition it would mean that 40 percent decomposition had occurred, close to the molecule for molecule appearance of peroxide and water suggested as possible by these authors. Mechanism I would call for an eight-fold increase of quantum yield for a decrease in light intensity of a hundred fold while II would call for a decrease under these conditions, of 20 percent. Obviously neither of these predict the experiments with the nicety of III, which calls for an increase of about 35 percent.

Temperature coefficient

The temperature coefficient predicted for the reaction by III is a function of the magnitude of $k_2/k_3^{\frac{1}{2}}$, and its rate of change with temperature. It will also vary with the light intensity, at least over some range of intensities, at a given tem-

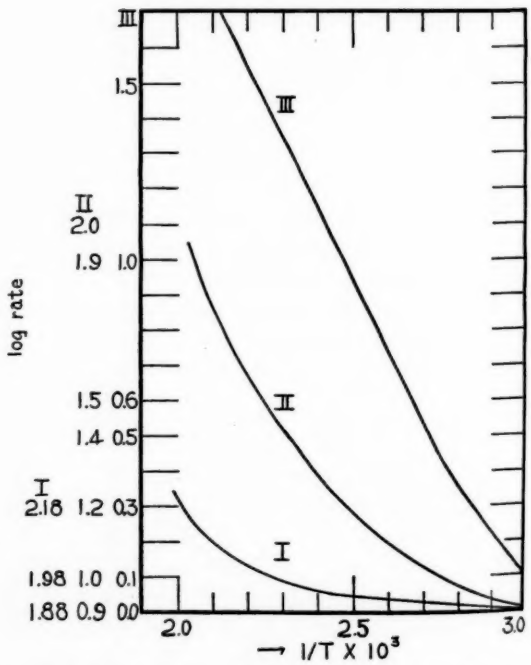

FIG. 2. Curve I, $I_{abs.}=100$; curve II, $I_{abs.}=10^8$; curve III, $I_{abs.}=1$. $Q_{III}=11.0$ cal.; $H_2=400$ mm; $O_2=200$ mm; $k_2/(k_3)^{\frac{1}{2}}=1.5\times10^{-3}$.

perature interval. Thus, if we neglect any temperature dependence of $I_{\text{abs.}}$, which would in general be smaller than usual temperature coefficients of chemical processes, the temperature sensitive term, involving $k_2/k_3^{\frac{1}{2}}$, if it is of the same order of magnitude or greater than the second term which we have assumed independent of temperature, may give rise to a high temperature coefficient. If, however, this term is small with respect to the second term, which would be true for small values of $k_2/k_3^{\frac{1}{2}}$ and high $I_{\text{abs.}}$, the temperature coefficient may be nearly unity. Any or all conditions in between these two should be possible. (Fig. 2.)

This immediately explains some of the difficulties which Marshall mentions in his paper. In studying the kinetics of the reaction he experienced little difficulty in obtaining reproducible results. When, however, he came to measurements of temperature coefficients he found that he could not obtain as good an agreement. For example with 3 amperes current through his arc he obtains a temperature coefficient of 1.13, with 5, 1.044, with 15, 1.038. These are obviously qualitatively what might be expected from Eq. III.

It becomes of interest to calculate the temperature coefficient if $k_2/k_3^{\frac{1}{2}}=1.5\times10^{-3}$. Reaction constants may be expressed

$$k=Z\gamma e^{-Q/RT},$$

where Z is a collision factor, γ a factor depending upon "steric" effects, and Q is the energy of activation of the process. Obviously, then

$$\frac{k_2}{k_3^{\frac{1}{2}}}=\frac{Z_2\gamma_2 e^{-Q_2/RT}}{(Z_3\gamma_3 e^{-Q_3/RT})^{\frac{1}{2}}}=1.5\times10^{-3}, \qquad \text{(a)}$$

$$e^{-QIII/RT}=e^{(Q_{3/2}-Q_2)/RT}$$

$$=\frac{(Z_3\gamma_3)^{\frac{1}{2}}1.5\times10^{-3}}{Z_2\gamma_2}, \qquad \text{(b)}$$

where $QIII=Q_2-Q_{3/2}$. Z_2 and Z_3 will be equal to the total number of collisions in the illuminated or reaction volume per minute divided by the number of collisions it takes to bring about the formation of 0.5 mm of peroxide. These can thus be calculated from the ordinary kinetic theory by using the equation for the number of collisions per second per cc.

$$Z=2(2\pi)^{\frac{1}{2}}N_1N_2\sigma_{12}^2\left(\frac{m_1+m_2}{m_1m_2}kT\right)^{\frac{1}{2}}\frac{\frac{1}{2}v60}{VN_{20}.5},$$

where

v = Volume illuminated (= 220 cc (Marshall)),
V = Total volume (= 1520 cc (Marshall)),
N = No. molecules per cc at 1 mm and 20°C,
N_1 and N_2 are the number of molecules in 1 cc at 1 mm pressure at temperature T.

The other symbols have their usual significance, and the Z's are expressed in mm colliding per mm pressure per sec.

If we use the value for σ of the oxygen molecule as that of HO_2, we obtain values for $Z_2=2.70\times10^8$ and $Z_3=5.9\times10^7$ at 60°C. And for any temperature,

$$Z_2=(16.0\times10^{11})/T^{\frac{1}{2}}, \qquad Z_3=(36\times10^{10})/T^{\frac{1}{2}},$$

since N_1 and N_2 will vary inversely as the temperature of the reaction vessel.

If we knew the values of γ_2 and γ_3 it would be possible to obtain from Eq. (b) $QIII$ exactly and thus express the variation of $k_2/k_3^{\frac{1}{2}}$ as a function of the temperature. These values, however, would be extremely uncertain since the fact that γ_3 appears to the half power would make the absolute magnitude of the γ's as well as the ratio of considerable importance in estimating the value of $QIII$. For example if $\gamma_2/\gamma_3^{\frac{1}{2}}=1$ ($\gamma_2=\gamma_3=1$) then $QIII$ would be 11.6 cal.; if $\gamma_2/\gamma_3^{\frac{1}{2}}=3$ ($\gamma_2=\gamma_3=9$), $QIII=10.6$ cal. Unfortunately, the one significant value in Marshall's data (that at 3 amp.) is the result of but a single experiment which, considering alterations in arc characteristics is not sufficient data upon which to base a value of $\gamma_2/\gamma_3^{\frac{1}{2}}$.

It becomes of interest to go briefly through the results of Salley and Taylor and see whether their anti-Arrhenius temperature coefficient agreed with a mechanism here postulated. At high temperatures there might, however, be other factors such as branching chains bringing about the large changes in temperature coefficient in short temperature intervals. A simple calculation, however (with $QIII=11.$ cal., $H_2=400$, $O_2=200$ $I_{\text{abs.}}=4$), will show that this would require that $(KT+10)/KT=1.12$ at 60°C, and $=1.26$ at 200° in disagreement with their observed values. It is

useless to speculate on this discrepancy with the present data on the temperature coefficient, which will be much more sensitive to changes in $k_2/k_3^{\frac{1}{2}}$ than is $I_{abs.}$ in Table I. A study of the change in temperature coefficient with concentration, light intensity and temperature, would give a definite answer.

It is well to note, however, that there are several facts arising from the data of Salley and Taylor, which are in semi-quantitative agreement with the theory. In the first place, the definite, but small increase in temperature coefficient with decreased mercury pressure is understood in light of a decrease in $I_{abs.}$. Also a marked increase in temperature coefficient with a decrease in light intensity, which only appears in the anti-Arrhenius region. Thus a comparison of the ratios of runs D_3 and D_4, H_4 and H_5, I_5 and I_6, all at different light intensities shows that the increase in rate for the same temperature interval goes up four to five-fold for a six-fold decrease in light intensity.

Objections to the theory

Aside from the lack of exact agreement with the temperature coefficients of Salley and Taylor noted in the last section the theory fits the results with considerable success. Objections may be raised that most of the measurements were conducted in flowing or circulating systems and hence that the assumptions of stationary states used in deriving the kinetics may not be valid. Marshall,[12] however, has been able to get similar, but not such exact results from a static system at 50°C. The low temperature, static experiments of Barak and Taylor,[13] are entirely unexplained. The author is inclined to the belief that in this case we are dealing with complex diffusion phenomena involving the alternate oxidation and reduction of mercury and mercuric oxide. An objection based on the fact that oxygen does not enter into the reaction kinetics equation (except in quenching) is certainly valid for some low pressure of oxygen. This can be allowed for by considering in the kinetics the possibility of hydrogen atom recombination. This leads to a complicated fourth degree equation in HO_2 with which it is not practical to deal. The lack of agreement of I with the results indicates that this does not concern us at higher oxygen pressures. The fact that Reaction II might be too strongly endothermic (32 cal.) to be worth considering would give some difficulty were the two hydrogen atoms adding to an oxygen molecule to give off an equal amount of energy (69 cal.). However, Professor Bodenstein has, in a private communication informed the author that according to some unpublished data the first goes on with the liberation of 40 cal., the second with 98 cal., which removes this objection.

[12] Marshall, J. Phys. Chem. **30**, 34 (1926).

[13] Barak and Taylor, Trans. Faraday Soc. **28**, 569 (1932).

Applications to Other Reactions

The theory of the reaction of hydrogen atoms and oxygen given here will have a bearing on the kinetics of many reactions. A mention should be made of the possibly necessary alteration of some of our ideas of the mechanisms of certain more important examples of these.

Hydrogen—carbon monoxide

A close parallel exists between the mechanism suggested and that advanced by Frankenburger[14] for the mercury sensitized formation of formaldehyde and glyoxal from hydrogen and carbon monoxide. The analogous reactions as given by our mechanism would be

$$H+CO \rightarrow HCO, \quad (1c)$$

$$HCO+H_2 \rightarrow H_2CO+H, \quad (2c)$$

$$HCO+HCO \rightarrow (HCO)_2, \quad (3c)$$

$$HCO+HCO \rightarrow H_2CO+CO. \quad (4c)$$

Reaction II, it is claimed by him, does not take place, and, indeed, the fact is substantiated by a quantum yield less than 2 aldehyde groups per quantum. He suggests (1c), (3c) and (4c) as the mechanism.

Hydrogen chlorine reaction

The author has already given the bearing on this reaction of the necessity of allowing HO_2 formation to take place in a bimolecular reaction between a hydrogen atom and an oxygen molecule. The success of the same assumption in the present work only serves to emphasize the importance of taking this into account in the

[14] Frankenburger, Zeits. f. Electrochemie **36**, 757 (1930).

theoretical treatments of the effect of oxygen on the hydrogen chlorine reaction. In the earlier discussion it was shown that the reaction

$$H+O_2 \rightarrow HO_2 \qquad (1)$$

did not necessarily end a H_2-Cl_2 chain, since for example, the reaction

$$HO_2+H_2 \rightarrow H_2O_2+H \qquad (2)$$

propagated the chain. The chain can, however, now, quite definitely be broken by reaction (3)

$$HO_2+HO_2 \rightarrow H_2O_2+O_2 \qquad (3)$$

but only some fraction of the atoms removed by (1) really result in broken chains.

Photodissociation of hydrogen peroxide

This reaction has been treated in papers by von Elbe and Lewis[15] and von Elbe.[16] Their theoretical discussion is based entirely upon the mechanism of Haber and Bonhoeffer which, as we can see, is wrong. The author offered cogent reasons why this mechanism should not be so completely accepted when von Elbe presented his work at the Buffalo meeting in 1931. My objection was based upon the earlier work of Bates and Taylor,[17] and of Marshall. The fact that the mechanism of Haber and Bonhoeffer is not definitely proven is also mentioned by Frankenburger and Klinkhardt in their final paper on this subject. It is quite obvious that in the light of the present work this subject is opened for a complete reconsideration.

The "anti-Arrhenius" temperature coefficient

The appearance of an "anti-Arrhenius" temperature coefficient in a reaction has been used as a criterion for the existence of a long chain. It would appear that this should be used with caution, since the mechanism suggested here gives one when the "chain" part of the reaction rises from an extremely small value to unity.

Oxidation processes in general

It is quite well to note that in suggesting that the oxidation of hydrogen atoms,—the simplest process of oxidation,—goes through the intermediate peroxide, HO_2, we are bringing this oxidation in agreement with numerous others[18] in which the peroxide intermediate has been detected. Of more specific interest is the bearing this bimolecular peroxide formation has on the oxidation of methyl groups studied by Bates and Spence.[19] They attempt to disprove the possibility of intermediate peroxide formation by showing the lack of effect of excess nitrogen on their reaction, assuming that the nitrogen would tend to stabilize the bimolecularly associated peroxide (CH_3O_2). This study, of course, proves nothing inasmuch as the methyl peroxide will probably need no such third body, if HO_2 needs none. Thus, it must be remembered that either of the two mechanisms, involving peroxide or hydroxyl, are equally well substantiated by their experimental results.

The evidence which has been offered that the mechanism suggested by Haber and Bonhoeffer cannot be the true one at low temperatures does not of necessity rule out the possibility of the more important postulates of these authors being involved in the high temperature or explosive reaction of hydrogen and oxygen. For example, although the intermediate hydroxyl group which is characteristic of their mechanism and which is spectroscopically found in hydrogen oxygen flames, is ruled out in the mechanism suggested, there is always the possibility of these being formed at the higher temperatures.

[15] von Elbe and Lewis, J. Am. Chem. Soc. **54**, 552 (1932).
[16] von Elbe, J. Am. Chem. Soc. **55**, 62 (1933).
[17] Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).
[18] Callendar, Engineering **123**, 147, 182, 210 (1927). Bone and Hill, Proc. Roy. Soc. **A129**, 434 (1930), etc.
[19] Bates and Spence, J. Am. Chem. Soc. **53**, 1689 (1931); Trans. Faraday Soc. **123**, 468 (1931).

Diffusion and Electrolytic Conduction in Crystals (Ionic Semiconductors)

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In the present paper a mechanism of diffusion and electrolytic conduction in solids is discussed, which is based on a formal treatment given by Frenkel. It is assumed that in a crystal in thermal equilibrium some of the atoms or ions are removed from their normal positions in the lattice to irregular ones in the interlattice space. Then diffusion and electrolytic conduction is possible by two processes; first by migration of the ions in the interlattice space, second by migration of the vacant places. The number of ions in the interlattice space can be calculated. If one considers the influence of polarization the result agrees in the order of magnitude with the observed data. It is also shown that the activation energy connected with the processes of movement is of the correct order of magnitude. Thus a satisfactory explanation of the exponential factor occuring in the empirical conductivity (or diffusion) formula is obtained. The constant factor multiplying the exponential can be explained at once for one group of cases; for the other group, where the constants apparently are too high, a tentative explanation is proposed.

THE experimental results[1] concerning diffusion and electrolytic conduction in crystals have led to the following conclusions: Diffusion and mobility of each kind of ions is represented by a term

$$Ae^{-B/T}. \tag{1}$$

This holds for ions in ionic crystals as well as for atoms in metals. Thus the (electrolytic) conductivity of binary compounds is generally given by

$$\kappa = A_1 e^{-B_1/T} + A_2 e^{-B_2/T}.^2 \tag{2}$$

Often one term is negligible compared with the other. This means that practically only one kind of ion can move.

Now the most obvious explanation of this empirical formula, given by different authors is the following; the constant B, multiplied by Boltzmann's constant k represents the minimum energy that an ion needs to be able to leave its position, while A depends upon the mobility of a single ion, the ionic concentration, and in the case of conductivity the ionic charge. A more detailed discussion of the mechanism always involves these general ideas. If the theory is to be satisfactory it must at least yield the right order of magnitude of the constants involved, and at this point serious trouble arises.

One might expect for the work function $B \times k$ a value of the order of magnitude of the lattice energy of a single ion, about 5–10 electron-volts. Actually one finds values between about 1/20 and 2 volts. These values are so much smaller than the lattice energy that it has been suggested[3] that the process of motion would not occur in the lattice at all, but would be limited to inner and outer surfaces. This conception might remove the difficulties concerning the constant B, but it leads to quite impossible values for the constant A.[4] For instance, in some cases one would have to assume values for the ionic velocities in the neighborhood of that of light. So both from a theoretical and from an experimental point of view[4] this hypothesis must be abandoned, though a certain influence of the above mentioned surfaces on the conductivity is not necessarily excluded.

Using a model that certainly does not correspond to the actual conditions but which allows a calculation of the maximum value of the

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[1] A survey of the field of electrolytic conduction is given by A. Joffé, *The Physics of Crystals*, New York, 1928; G. v. Hevesy, Handbuch d. Physik **XIII**; C. Tubandt, Handbuch d. Exp. Physik **XIII**, 1 (1932); W. Jost, Müller-Pouillets Lehrbuch d. Physik **IV**, 4. In print.

[2] First observed experimentally by T. E. Phipps, W. D. Lansing and T. G. Cooke, J. Am. Chem. Soc. **48**, 112 (1926).

[3] A. Smekal, Phys. Zeits. **26**, 707 (1925).

[4] Discussion: see W. Jost, Zeits. f. physik. Chemie **B6**, 88, 210 (1929); **B7**, 234 (1930); A. Joffé, Zeits. f. Physik **62**, 730 (1930).

mobility, I have shown[5] that if one accepts the above interpretation of the exponential the maximum value of the constant A should be $A_{max} \sim 20-100$, if the conductivity κ is measured in ohm^{-1} cm^{-1}. For many cases the observed values are smaller than A_{max}, but in a number of cases A has values up to 10^6. As long as this discrepancy is not removed the interpretation of the exponential factor in Eq. (1) also remains in doubt. In the present article we will attempt to show that when one takes into account the polarization forces which come into play when an ion is moved from a regular to an irregular position in the lattice, one obtains B values of the observed order of magnitude. Furthermore, by means of a more refined treatment of the ionic diffusion process, the discrepancies in the A values can be formally removed. The most logical and detailed theoretical treatment of these problems that exists so far has been given by Frenkel.[6] He considers all possible processes, though his reasoning is rather formal and does not lead to numerical values of the exponential that could be compared with experiments. Nevertheless we can base our discussion on it.

Frenkel's treatment is based on the following considerations:

(1) An atom (or ion) with sufficient energy, for instance the atom a in Fig. 1, can be removed from its normal place to a metastable equilibrium position b in the "interlattice space," producing in this way a hole at a. In thermal equilibrium a certain number of atoms will be in the interlattice space and a corresponding number of holes will be left in the lattice.

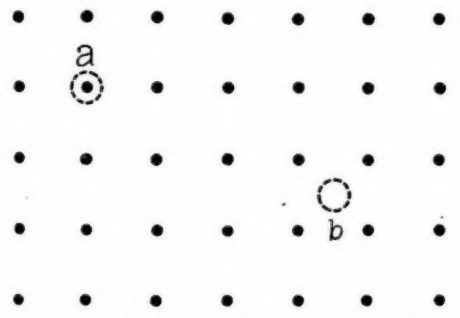

FIG. 1. Schematic representation of the diffusion and conduction process according to Frenkel: normal positions in the lattice and metastable positions in the interlattice space at b.

(2) Two processes can cause diffusion or conductivity: (a) A neighboring ion with sufficient energy can jump over a potential barrier into one of the holes, and a second one can jump into the hole left by the first, etc. Frenkel calls this diffusion of the vacant places. (b) An ion in an irregular position b can jump over potential barriers to other irregular positions or to a vacant place, corresponding to a regular position.

Both processes, movement of the vacant places and movement of a particle in the interlattice space give diffusion and electrolytic conductivity. First we have to obtain an expression of the equilibrium concentration of the holes. One migh expect, if n is the number of holes per unit volume, N the number of regular places per unit volume and E the "hole energy," that this concentration would be proportional to $e^{-E/kT}$. Frenkel showed, however, by kinetic reasoning, that one gets instead

$$n \sim N e^{-E/2kT}, \tag{3}$$

a rather important result.[7] As Frenkel explains, the involved process is analogous to the dissociation of a diatomic molecule. An atom in a regular position "dissociates" into an atom in an irregular position and a vacant place; later an atom in an irregular position can recombine with the vacant place to form an atom in a normal place. It seems worth while to show the validity of this result by a statistical treatment. We consider two sets, each of N cells, the one representing the regular places in the lattice, the other the irregular places in the interlattice space (their number can be different from that of the normal places, but this would not change the general form of the result). We distribute N particles among them. The number of particles in the normal places may be n_0 and in irregular places n_1, where $n_0+n_1=N$.

[5] W. Jost, Zeits. f. physik. Chemie **B16**, 129 (1932).

[6] I. Frenkel, Zeits. f. Physik **35**, 652 (1926). Of other contributions to this field we mention: H. Braune, Zeits. f. physik. Chemie **110**, 147 (1924); W. Braunbek, Zeits. f. Physik **44**, 684 (1927). S. Dushman and I. Langmuir, Phys. Rev. **20**, 113 (1922); **22**, 357 (1923). A. van Liempt, Rec. Trav. Chim. **51**, 114 (1932).

[7] It is remarkable, that in the theory of electronic semiconductors the same expression is obtained. See A. H. Wilson, Proc. Roy. Soc. **A133**, 458 (1931); **134**, 277 (1931). R. Peierls, Ergebnisse der exakten Naturwissenschaften **11**, 317 (1932).

Among the n_0 particles let there be n_0^i with energy ϵ_0^i, and among the n_1 particles, n_1^i with energy $E+\epsilon_1^i$, where $i=0, 1, 2\cdots$ and

$$\sum n_0^i=n_0; \quad \sum n_1^i=n_1.$$

$$\sum n_0^i\epsilon_0^i+\sum n_1^i(E+\epsilon_1^i)=E_0.$$

Now the number of distributions of n_0 particles over N cells and n_1 particles over another N cells is

$$W=\frac{N!}{n_0!(N-n_0)!}\frac{N!}{n_1!(N-n_1)!}=\frac{(N!)^2}{(n_0!)^2(n_1!)^2},$$

if we put not more than one particle in each cell and if we do not distinguish between different particles. Should we distinguish between different atoms, this would have to be multiplied by $N!$, and this being a constant would not affect the following results. Then the number of ways of selecting n_0^i particles out of n_0 and n_1^i out of n_1, respectively, are (the particles are now distinguished by their positions in different cells)

$$W_0=n_0!/\prod_i n_0^i!,$$

and

$$W_1=n_1!/\prod_i n_1^i!,$$

and so the entire number of complexions

$$W_e=(N!)^2/n_0!n_1!\prod n_0^i!\prod n_1^i!.$$

Determining the maximum of W_e under the above conditions, we obtain

$$n_0^i=(1/n_0)e^{\alpha}e^{-\beta\epsilon_0^i}; \quad n_1^i=(1/n_1)e^{\alpha}e^{-\beta(E+\epsilon_1^i)}$$

and

$$n_0=\sum n_0^i=(1/n_0)e^{\alpha}\sum e^{-\beta\epsilon_0^i};$$

$$n_1=\sum n_1^i=(1/n_1)e^{\alpha}e^{-\beta E}\sum e^{-\beta\epsilon_1^i};$$

thus

$$n_1^2/n_0^2=e^{-\beta E}(\sum e^{-\beta\epsilon_1^i}/\sum e^{-\beta\epsilon_0^i}).$$

Now for the first approximation we can assume $n_0\sim N$ and $\epsilon_0^i\sim\epsilon_1^i$. This gives $n_1\sim Ne^{-E/2kT}$, $\beta=1/kT$ in accordance with Frenkel's result (Eq. (3)).

So for comparison with experiment we need consider only 1/2 of the calculated "hole energy." But this value $E/2$ generally will not be the only term in the exponent. For only a fraction of the ions in irregular positions or around holes can move because they have to surmount a potential barrier U. In both cases the total number of ions which move in diffusion and conduction processes is proportional to

$$e^{-(E/2+U)/kT}. \tag{4}$$

Before we derive values for E and U, we shall give an approximate expression for diffusion and electrolytic conductivity in case *a* and *b*.

The number of ions in the neighborhood of a hole depends on the lattice type, and is often between 4 and 8. Since the present calculations cannot give more than the correct order of magnitude, we shall assume the total number of ions around holes to be $6n_1$. We assume that the fraction $e^{-U/kT}$ of these ions can jump into holes. If the distance of an ion from the hole is d, and its average velocity is v, the mean thermal velocity, the diffusion constant is approximately $D=dv/2$. Our particles can move only in one direction, but the group of 6 particles around a hole is almost equivalent to one particle, capable of moving in every direction. Thus we obtain as the rate of diffusion near the holes

$$D_h=\tfrac{1}{6}(dv/2)e^{-U/kT}.$$

The average diffusion constant for all particles is given by this expression multiplied by the fraction of ions around holes, which is $6n_1/N$. So we obtain finally

$$D=\tfrac{1}{6}(dv/2)e^{-U/kT}\cdot 6\cdot e^{-E/2kT}$$

$$=(dv/2)e^{-(E/2+U)/kT}.$$

Using as approximate numerical values $d=3\times10^{-8}$ cm, $v=5\times10^4$ cm sec.$^{-1}$, we obtain

$$A=dv/2=7.5\times10^{+4}\text{ cm}^2\text{ sec.}^{+1}\sim65\text{ cm}^2\text{ day}^{-1},$$

as maximum value for A in case of diffusion, in accordance with many of the experiments. To obtain the expression for electrolytic conductivity we may use Einstein's relation

$$D=BkT,$$

where B is the mobility of the ions, and the relation

$$\kappa=n(ze)^2B,$$

where n is the number of ions per unit volume and ze the charge of one ion. The result is

$$\kappa=[n(ze)^2\cdot d\cdot v/2k\cdot T]e^{-(E/2+U)/kT}.$$

The factor before the exponential is practically identical with that derived by the classical electronic theory of metals, and has a numerical value of the same order of magnitude as D (when expressed in $cm^2\ day^{-1}$), as can be shown by putting in reasonable numerical values. The value of κ is then of the order of magnitude

$$\kappa \sim (10-100)e^{-(E/2+U)/kT},$$

as mentioned above. For the motion in the interlattice space we would obtain practically the same expression. In regard to the application of Einstein's formula we refer to a paper of C. Wagner[8] and mention that our formula for κ could have been derived without Einstein's formula by using Braunbek's[9] method, which also would show that Ohm's law holds within rather wide limits. Of course one could easily obtain more accurate numerical factors by considering special crystal lattices. For instance if we consider particles which can move only in 3 mutually perpendicular directions, our above expression for D would be smaller by a factor $\frac{1}{3}$. Considering the uncertainty of any special assumptions a more accurate treatment is as yet not justified.

The next step is to obtain an expression for the energy E required to move an ion from a regular to an irregular position.[10] To do this we have to consider a special lattice type. As the first example we choose the NaCl-type of lattice. In this case we can obtain in a very simple way a rough value of the "hole energy" E. Suppose that an ion, say at 0, 0, 0 (Fig. 2) is removed to a point $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ in a distant cell. Suppose the new position is so far away from the original one that the potential of the displaced ion at that point can be neglected. This means that in the expression for the potential energy of the displaced ion we can neglect the

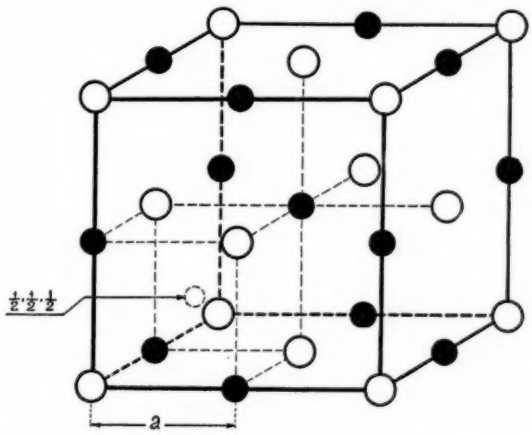

FIG. 2. Sodium chloride lattice normal positions and positions in the interlattice space at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, etc.

presence of the hole and of ions in the interlattice space and obtain this energy merely by a summation over all ions in normal positions. The Coulomb part of the potential energy of the ion in its normal place is $-1.74e^2/a$, where a is the interionic distance. Its Coulomb energy in the interlattice space at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ is zero, because it is surrounded quite symmetrically by positive and negative ions; thus the work function would be $+1.74e^2/a$, this is about 8–10 electron-volts. If we should consider the repulsive forces this value would increase to about $2.27e^2/a$. Both values are much higher than the experimentally observed ones. $E/2+U$, where U is the potential barrier, is about 1 volt for the cations of the alkali and silver halides.

Now it has been pointed out by Fajans[11] and Reis[12] that there is a correlation between electrolytic conductivity in crystals and polarizability and polarizing properties of the ions. Thus the work function for a small ion like Ag^+ would be smaller than that of ions of high polarizability, whereas that of anions with high polarizibility would be correspondingly larger. This gives an explanation of the fact that very often only one kind of ion is mobile. But quantitative calculations on this basis have never been carried through. It has even been concluded by some authors that such an influence could be important only for ions at surfaces, because only in asym-

[8] C. Wagner, Zeits. f. physik. Chemie **B11**, 139 (1930).

[9] W. Braunbek, Zeits. f. Physik **44**, 684 (1927).

[10] Work functions, so called "Platzwechsel-energies" have been calculated before, by Rogowski (Arch. f. Elektrotechnik **18**, 123 (1927); and by Braunbek.[9] But both of them derived them for the displacement of the lattice of the positive ions as whole towards the negative ones. Though this calculation for Rogowski's purpose was justified—discussion of the electrical breakdown—its results cannot be used for the process of electrolytical conduction and diffusion which we consider.

[11] K. Fajans, Fortschr. d. physikal. Wissensch. (russ.) **V**, 294 (1926).

[12] A. Reis, Zeits. f. Physik **44**, 353 (1927).

metrical fields the polarization energy can reach considerable values. It is obvious that this conclusion is quite wrong. For it is quite unimportant if there exist any initial asymmetrical fields but it is only necessary that such fields be produced in the process of motion: and just this occurs in our case. In the final state we have asymmetrical fields both around the hole and around the ion in the interlattice space. In these fields the polarization energy can become very large, even great enough to compensate practically the whole work function computed only from the Coulomb forces.[13]

For this first estimate we use an expression for the polarization energy obtained by treating the crystal as a continuum* (more exact treatment below). If r_0 is the radius of an ion, considered as a sphere, its electrostatic energy in vacuum is $\frac{1}{2}e^2/r_0$; if we bring it into a medium of dielectric constant ϵ, its energy becomes $\frac{1}{2}e^2/r_0\epsilon$. The polarization energy is evidently the difference between the two

$$E_{\text{pol}} = -\tfrac{1}{2}e_2/r_0((\epsilon-1)/\epsilon).$$

Since a polarization arises around the hole as well as around the displaced ion (now a hole is equivalent to a charge of sign opposite to that of the displaced ion) this polarization energy occurs twice, we have

$$E_{\text{pol}} = -(e^2/r_0)((\epsilon-1)/\epsilon).$$

If we take $r_0 = a/2$ and $\epsilon = 6$[14] we obtain

$$E_{\text{pol}} = -1.67e^2/a,$$

an expression of the same order of magnitude as the Coulomb potential. Thus the final work function becomes

$$E \sim 0.6e^2/a \sim 2.5 \text{ volts}$$

which agrees quite well with observed values.

Of course, this can be considered only a rough approximation. But even this approximation is sufficient to account for the phenomenon of unipolar conductivity. In NaCl at low temperatures and in silver halides generally only the cations can move. Now the radii of these cations are smaller than those of the anions; this gives a different value in the repulsive and polarization potential for anions and cations, favoring the mobility of the cations.

It is interesting to investigate a salt of high electrolytic conductivity, for example α-Ag_2S, stable above 179°C. We choose silver sulphide,[15] since it is one of the few salts (the α-modifications of Ag_2S, Cu_2S, AgJ, CuJ, CuBr) of extremely high electrolytic conductivity (conductivity as high or higher than that of the best aqueous electrolytes!) for which the lattice structure is known. It crystalizes in the fluorite type of lattice; from the density we take the distance between two silver ions as $a = 3.05$A.

First we compute the electrostatic energy necessary to produce a hole in the following way (see Fig. 3).[16] (A Cartesian coordinate system is placed with its origin at the center of the unit cell of our lattice having its axes parallel to the crystallographic axes.) Let a silver ion, say at

[13] M. Born (Zeits. f. Physik **79**, 62 (1932)) has lately discussed in a similar case the "hole energy," in connection with the discrepancy between the theoretical value for the energy of the photographic primary process and the empirical value as determined by Pohl and coworkers. Although in this process the polarization energy in the neighborhood of two neutralized atoms is not quite negligible, it is not mentioned by Born. However, in this case the polarization energy is of a smaller order of magnitude than in ours, because the assymmetrical part of the field, produced by neutralizing two neighboring ions can be represented by a dipole field which decreases much more rapidly with the distance than the assymmetrical Coulomb fields around a hole and around a displaced ion at a distant point in the interlattice space. See, however, W. Klemm, Zeits. f. Physik **82**, 529 (1933).

* See also M. Born's calculation of the heat of hydration of ions (Zeits. f. Physik **1**, 45 (1920)) and K. F. Herzfeld's discussion Handb. d. Physik **22**, 424, Berlin (1926).

[14] In the case of the silver halides ϵ is >10!

[15] Unfortunately the nature of the conductivity of silver sulphide is still under discussion (W. Jost u. H. Rüter, Zeits. f. physik. Chemie **B21**, 48 (1933). C. Wagner, Zeits. f. physik. Chemie **B21**, 25 (1933). We can, however, avoid any of these difficulties by basing our discussion on the rate of diffusion which has been measured for copper ions in small concentrations in silver sulphide (H. Braune, Zeits. f. physik. Chemie **112**, 270 (1924); C. Tubandt, H. Reinhold, Z. anorg. Chem. **177**, 253 (1928); W. Jost u. H. Rüter, Zeits. f. physik. Chemie **B21**, 48 (1933). From Braunes measurements we take the diffusion constant

$$D = 10 \times e^{-1610/T} \text{ cm}^2 \text{ day}^{-1}.$$

This velocity is as high or higher than that of salts in aqueous solutions!

[16] Holes can also be produced by removing ions to surfaces. But as long as only ions of one type are removed this would give an amount, depending on the size of the surface. Such a process, though it might occur, could not be identified with the generally observed conductivity.

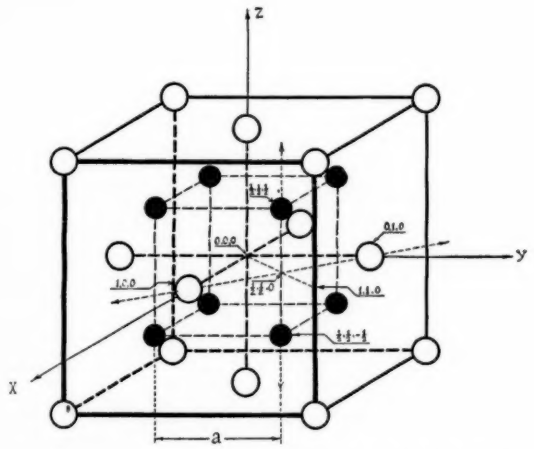

FIG. 3. Silver sulphide (fluorite type of lattice). Normal positions and positions in the interlattice space at 0, 0, 0, etc. Solid circle, silver ions; circle, sulphur ions.

$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ be displaced into the center of a distant complete unit cell, equivalent to the origin 0, 0, 0. Suppose again the new position is so far away from the original position, that we can obtain the potential energy by a summation over all ions in normal positions. The work function E is the difference between the normal lattice energy of a silver ion and the energy of the displaced silver ion in the irregular position 0, 0, 0 with all lattice points in the neighborhood regularly occupied. In the calculation of this energy difference we need only consider in the summation the groups of ions for which the potential at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, is appreciably different. Although the two individual summations need not converge to the respective lattice energies their difference is independent of the mode of summation. Carrying through this summation for the first 38 negative and the first 55 and 56 positive ions respectively (since in the first case the potential of the ion $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ on itself has to be omitted) we obtain as electrostatic potential energies of an ion at

$$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \qquad 0, 0, 0,$$

$$-10.289\, e^2/a + \text{const.} \qquad -7.981\, e^2/a + \text{const.}$$

$$\Delta E_{\text{Coul}} = +2.308\, e^2/a.$$

The separate contributions to Δ of the following positive and negative ions can be neglected as was tested by a further summation. By consideration of the repulsive forces this energy would decrease slightly (see below), but still its value would be about 9 electron-volts, much higher than the experimental value, which in the case of silver sulphide must be of the order of magnitude of 0.1 volt.

Again the discrepancy can be removed by consideration of the polarization energy. The expression for the polarization energy is

$$E_{\text{pol}} = -\sum[(\alpha_-)/2(F_-^{i})^2 + (\alpha_+)/2(F_+^{i})^2]$$

where α_- and α_+ are the respective polarizabilities of anions and cations and F_+ and F_- are the field strengths at the positions of the respective ions. The summation must be extended over the neighborhood of the hole and over that of the ion in the interlattice space, where again the assumption is involved that the distance between the hole and the displaced ion is large. For the field strengths F besides those produced by the silver ion (in the neighborhood of the hole the field is equivalent to that of a negative charge in the original position of the removed silver ion; but because it appears in the square we can as well take the field of one silver ion) we have to consider those produced by the induced dipoles. It is almost impossible to do this exactly. Thus we computed first the polarization energy neglecting the fields of the induced dipoles. To take into account this effect and the fact, that the polarizability in the inhomogeneous fields in the neighborhood of ions would be smaller than that observed in homogeneous fields, we take only one-half of the above polarization energy. This assumption was tested by considering roughly the dipole fields; furthermore the value obtained in this way is almost identical with that obtained by treating the crystal as a homogeneous dielectric. Carrying through the summation in the neighborhood of a hole and of an ion in the interlattice space we obtain for the polarization energy

$$E_p = -(9.3\alpha_- + 16.2\alpha_+)e^2/a^4.$$

In addition we have to consider the potential of the repulsive forces. We use Born's expression for this potential between a silver and a sulphur ion, we have

$$E_{+-} = +1/9 \times 0.63(e^2 r_0^8/r^9)$$

where r_0 is the equilibrium distance in the lattice

and where the numerical factor is obtained by means of the equilibrium condition for the lattice (only repulsive forces between a sulphur ion and the nearest silver ions have been considered, which is allowable in the first approximation). For the repulsive potential between two silver ions we have a corresponding expression

$$E_{++}=0.29e^2\sigma^8/9r^9,$$

where σ is the diameter of a silver ion, taken from Goldschmidt's data. The numerical factor is taken from the NaCl type of lattice; this means that we assume for the repulsion between two silver ions at a distance equal to the sum of their radii the same expression that holds for the forces between an alkali and a halogen ion.[17] We obtain for the increase of the repulsion potential for an ion, attending its removal from a normal place to a place in the interlattice space

$$\Delta E_{\text{rep}}=-0.11(e^2/a).$$

In the expression for the polarization energy we have to express α in units of a^3. With the data given by Van Vleck[18] and dividing the final expression by 2 we obtain $E_p=-2.15e^2/a$.[19]

Finally we obtain for the complete work function associated with the displacement of an ion from its normal position into the interlattice space

$$E=\Delta E_{\text{Coul}}+\Delta E_{\text{rep}}+E_p=(2.31-0.11-2.15)e^2/a$$
$$=+0.05e^2/a\sim 0.24 \text{ electron-volts},$$

which is of the same order of magnitude as the observed value for $E/2+U$ (U potential barrier) 0.14 volt. Of course this result is only an approximate value, but in any case it shows that the work function is small. One must not conclude that a small or even negative value of the work function would mean instability of the lattice, and therefore be physically impossible. For our main assumption was that in the neighborhood of a vacant place there was no other vacant place. This means that only a certain small fraction of ions can be removed with so little energy, for the succeeding ones more energy would be required. In any case we may conclude from our calculation that the work function is small compared with the lattice energy, and this is just what follows from the experiments.[20]

The last step that still remains is to find a value for the height of the potential barriers connected with the motion either of an ion near a hole or in the interlattice space. It can be shown that these values are also small compared with the lattice energy, though the accuracy of our calculations is not yet sufficient to give full agreement with the observed values in the case of Ag_2S. This is as much as we can expect for the present.

Let us first consider a vacant place, let as say at $-\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{1}{2}$ (see Fig. 3). Suppose that a silver ion at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ jumps in a straight line into this vacant place. On its way it has to pass two equal potential barriers whose height depends chiefly upon the repulsive forces of the surrounding negative ions. These maxima are

[17] This approximation for the repulsive potentials may be not very good. But the inaccuracy certainly lies within the limits of other approximations we have made, and a more accurate treatment would be worth while only if a much better approximation could be obtained. This would require that besides considering van der Waals forces (M. Born and J. E. Meyer, Zeits. f. Physik **75**, 1 (1932)) one would have to abandon the simple expression for the repulsive forces consisting of an inverse power or an exponential function of the distance. Both assumptions are too rough for such a close approach of the ions though they allow one to calculate good values for the equilibrium energy of the lattice. And furthermore one would have to consider the displacement of ions in the neighborhood both of holes and of migrating ions. Moreover the polarizability may not be assumed to be constant. See also J. E. Meyer, J. Chem. Phys. **1**, 327 (1933).

[18] Van Vleck, *Electric and Magnetic Susceptibilities*, Oxford, 1932.

[19] By using the expression for a continuous dielectric, as we did above, we should obtain for the polarization energy $\backsim -2.4\ e^2/a$, if we use Goldschmidt's data for the radius of the Ag-ion, and for the dielectric constant $\epsilon=10$ (this corresponds about to the value for AgCl; the dielectric constant of Ag_2S has not been measured, but cannot be smaller than this value).

[20] In the case, where the work function is almost zero, we may assume for the present approximation that a certain fraction of ions is removed from regular places, depending only very little on temperature, whereas it would require much higher energy to remove more ions. It is noteworthy that this result is equivalent to a picture given by G. C. Schmidt (Ann. d. Physik **80**, 605 (1926)). He assumed for the explanation of the experimentally found unipolar conductivity, that the crystal is built up of complex molecules, from which only one ion can dissociate with little energy.

reached in the neighborhood of the points $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ and $-\frac{1}{3}, -\frac{1}{3}, -\frac{1}{3}$, and have values of about $0.1e^2/a$. But this is not the maximum of the potential in the path of the ion. At the point 0, 0, 0 the potential energy has a higher value, which we can compute approximately. We have already calculated the difference in Coulomb potential for $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and 0, 0, 0 when all surrounding positions are occupied. This was $+2.3e^2/a$.

If we now consider repulsive forces and the fact that initially $-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}$ is unoccupied, and then during the displacement both this place and the position $+\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ are unoccupied, we obtain $\Delta E = \sim 0.45e^2/a$, where the change in polarization energy is neglected, which, as an approximate calculation showed, certainly would not decrease this value. Though this value is of the usually observed order of magnitude, about 2 volts, it is too high for the case of silver sulfide. Thus it seems more probable that motion in the interlattice space is the actual process occurring in the case of silver sulfide. However, our calculations do not exclude the first process. It is readily seen that they must yield a result which generally is too high. For we have regarded the surrounding ions as remaining fixed in the lattice, whereas indeed by any perturbation such as that produced by a displaced ion or a hole, they will tend to move to new equilibrium positions with lower potential energy.

Thus far we have considered only the motion of an ion from a normal position to another normal position which is vacant. Now we shall consider the migration of ions initially in abnormal lattice position at equilibrium. In this process the assumption that the neighboring ions are not displaced in the path of the migrating ion has to be abandoned. An ion in the interlattice space at 0, 0, 0 (see Fig. 3) may move to the equivalent point 1, 1, 0. Obviously it has to pass an energy maximum at $\frac{1}{2}, \frac{1}{2}$, 0 due to repulsive forces. If we should calculate the repulsive potential for this point we should obtain extremely high values, but these would not mean much because the applied formulae do not hold at such small distances. What really will happen if we bring a silver ion to $\frac{1}{2}, \frac{1}{2}$, 0 is that the silver ions at the neighboring points $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$ as well as the sulphur ions at 1, 0, 0 and 0, 1, 0 will be pushed aside in the direction of the arrows (Fig. 3.) Since not only these neighboring ions but also those in the distant surrounding would be displaced it is practically impossible to give an exact treatment. We shall first try to get an approximation by assuming reasonable displacements of the immediate neighbors and then calculate the work required for this displacement and the potential between a silver ion and the nearest surrounding ions.

We choose the displacement of the neighboring ions so that the repulsive potential is the same as for the ion in 0, 0, 0. This displacement is not very different from that which makes the distance between the migrating Ag-ion at $\frac{1}{2}, \frac{1}{2}$, 0 and the lattice silver ions equal to twice the radius of a silver ion, and the distance to the next sulphur ions equal to the normal lattice distance $a/2\,3^{\frac{1}{2}}$. We do not need to know these distances more exactly because in our later computation of the Coulomb potential they enter only with the first power. The assumed displacements are the following; $0.24a$ for the silver ions and $0.16a$ for the sulphur ions. The Coulomb potential at $\frac{1}{2}, \frac{1}{2}$, 0, if one neglects the displacements of the surrounding ions, differs from that at 0, 0, 0 by an amount $+0.16e^2/a$. If we consider in the change of potential produced by shifting the neighboring ions only the contribution of the above mentioned 4 nearest ions, we obtain an additional contribution $-0.26e^2/a$. Thus for the first approximation the change in the Coulomb potential and repulsive potential (the latter is zero!) becomes $\Delta E_1 = -0.10e^2/a$.

It remains to calculate the work required for the displacement of the four neighboring ions. We take a one dimensional model, a chain of alternating positive and negative ions, of which we take into account 12 ions of charge $\pm e$ (see Fig. 4). We displace the ions symmetrically from the center so that the distance between the middle ions becomes 1.5 times the original distance a and that between each other pair of neighboring ions $0.95a$. We compute the change in potential energy assuming Coulomb and repulsive forces. Using Madelung's[21] potential and the inverse ninth power for the repulsive

[21] E. Madelung, Phys. Zeits. **19**, 524 (1918).

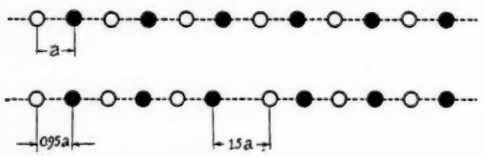

FIG. 4. One-dimensional model representing the deformation of the lattice by a migrating ion.

potential we find by means of the equilibrium condition for the latter $0.69e^2a^8/9r^9$.

Then we find for the change in potential energy for the above displacement, considering the Coulomb forces between every pair of the 12 ions and the repulsive forces between each pair of neighboring ions $\Delta E=0.18e^2/a$. The compression could actually be distributed over a still longer chain of ions, which would decrease the required energy even more. We assume, that this value also gives the right order of magnitude for a three dimensional model, for which we assume as an approximate value $\Delta E_2=0.2e^2/a$. The sum of this energy and the Coulomb contribution ΔE_1 yields the following value for the potential barrier

$$U\sim 0.1e^2/a\sim 0.45 \text{ e.v.},$$

as long as we neglect the change in the polarization energy, which could not be great. In the above we have arbitrarily determined the displacements in a way that allowed simple calculations, whereas they should be determined to give a minimum value of the barrier. Though this minimum problem cannot be solved without a prohibitive amount of labor, the result obtained with the assumed approximations makes it probable that the proposed mechanism accounts satisfactorily not only for the generally observed order of magnitude of the barrier but also gives fair agreement with the actual values in the case of silver sulfide. The observed value for $E/2+U$ in this case is 0.14 e.v., our calculations give 0.6 volt. Better agreement than one of order of magnitude can not be expected.[22]

To show that the special properties of Ag_2S are necessary to obtain a work function of almost zero we give here the approximate value for Na_2S, which is isomorphous with Ag_2S, with an interionic distance of 3.26A. The main difference in the work function is caused by the difference in the polarization energy, which depends on the larger interionic distances and the smaller polarizability of the sodium ion compared with the silver ion.[23] For the polarization energy we obtain with the same assumptions as above $E=-1.42e^2/a$.

This is smaller (in its absolute value) than for the case of silver sulphide by about $0.7e^2/a$, and this difference accounts at once for the generally observed small conductivities of alkali compounds as compared with the analogous silver compounds (the conductivity of Na_2S has not yet been measured). By an approximate calculation of the work function for sulphur ions in case of silver sulphide we can easily account for the experimental fact of unipolar conduction.

The formal manner in which A-values higher than about 100 could be explained[24] may be mentioned at this point.* There seems to be

[22] We have not yet discussed the mechanism of transfer of an ion between normal positions and abnormal ones in the interlattice space. It may happen that the potential barrier, which an ion must cross is greater than the energy difference between its initial and final positions. Apparently this additional potential barrier is unimportant for electrolytic conduction, which depends only on the equilibrium concentration of ions in the interlattice space. However, for diffusion this barrier is quite important, because in the process of concentration equalization the exchange of ions in normal positions and in the interlattice space has to be considered. It is necessary, that the microscopic equalization occurs in a time interval very small compared to the time required for the propagation of ions over observable distances. For a detailed discussion one may refer to the treatment of an analogous problem given in a previous article (W. Jost, Zeits. f. physik. Chemie **B9**, 73 (1930)).

[23] Using the formula for a continuous dielectric to obtain approximate results, one would have to assume for r_0 in case of Na_2S a higher value than in the case of Ag_2S. For not the diameter of the cation is of importance, but the distance to the nearest surrounding ions.

[24] See also: W. Jost, Zeits. f. physik. Chemie **B16**, 129 (1932).

* *Note added in proof.* I am indebted to Professor K. F. Herzfeld for calling my attention to the fact that similar difficulties arise in the treatment of thermionic emission; the observed factor multiplying the exponential is sometimes of greater order of magnitude than the maximum theoretical value. This discrepancy has been attributed to the neglect of the temperature variation of the work function (see e.g., L. Brillouin, *Les Statistiques Quantiques*, Vol. II, p. 223, Paris, 1930). It is very probable that a similar situation exists in the case of electrolytic conduction since it is readily seen that the work function might vary considerably with temperature. In view of this fact one

only one possibility which is satisfactory, though it is not easily proved. If an ion, moving in the interlattice space, has enough energy to pass one energy barrier, then its energy is also sufficient to pass an infinite number of barriers as long as the energy is not used to excite lattice oscillations.[25] Thus one has to expect a variable free path, depending on this excitation function. If the expression for the mean free path λ were of the form

$$\lambda = f \cdot a \cdot e^{-U'/kT},$$

where f is a large number, then one would obtain a formula in agreement with the experiments without having unreasonable values for the actual free path as long as U' is large enough.

A second reason for a variable free path for the motion of a particle in the interlattice space if the following; because of the presence of "holes" and of ions in the interlattice space, which we neglected in the first approximation, the potential barriers will not all be of the same height, and a path which is short for an ion of low energy may be longer for an ion with higher energy. This suggests an exponential dependence on temperature of the sort already mentioned.

Of course one would also have to discuss the influence of holes and ions in the interlattice space on the work function, but a more detailed treatment does not seem to be justified as long as one cannot obtain much more accurate results. By the above calculations we have shown that for a model representing a motion of particles in the lattice one obtains reasonable values for the electrolytic conductivity and diffusion. For the present one cannot yet expect to obtain accurate numerical values. The agreement in order of magnitude seems to prove the correctness of our assumptions, and indicates that objections raised against a lattice process are not tenable. Of course our model as already mentioned by Schottky and Wagner[26] would permit an explanation of effects depending on perturbations of the lattice, if one assumes that at low temperatures thermal equilibrium is not always reached. For metals similar ideas would have to be assumed. Here holes in the crystal can be produced by removing particles to the surface, without transferring them into the interlattice space.[27] This process would also be possible with ionic crystals, but it is rather improbable; an effect not depending on the size of the surfaces could only be obtained by removing equal numbers of positive and negative ions, by building up new lattice structures outside the former surface.

is not justified in drawing general conclusions concerning the conduction mechanism from the observed deviations from a simple exponential relation.

[25] Compare A. v. Hippel, Zeits. f. Physik **75**, 145 (1932), who discusses the same question for electrons in the case of the electric breakdown of insulators.

[26] W. Schottky, H. Ulich u. C. Wagner, Thermodynamik S, 380 (1929); W. Schottky and C. Wagner, Zeits. f. physik. Chemie **B11**, 163 (1930); C. Wagner, Zeits. f. physik. Chemie. Bodenstein-Festband, S, 177 (1931).

[27] This means: extending the crystal beyond its original limits.

Diffusion of Hydrogen Through Platinum and Nickel and Through Double Layers of These Metals

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Flow of hydrogen through single sheets of Ni and Pt with atmospheric pressure on ingoing side and pressure of 0.1/mm on outgoing side follows the empirical equation

$$R = A \cdot ((p_0^{\frac{1}{2}} - p_t^{\frac{1}{2}})/x) \cdot T^{-\frac{1}{2}} \cdot \epsilon^{-b_1/T}$$

similar to that given by Borelius, where p_t is small compared with p_0 but apparently proportional to p_0; with double layers of these two metals the b_1 of the exponential is dependent *only on the metal at the outgoing surface*, and is the difference between the work of escape from the outgoing surface and the heat of solution of hydrogen in that metal. The kinetic theory flow equation is sufficient to explain the p_t, and the variation of p_t with temperature may be used to compute the work function at the outgoing surface, and also to obtain values of m/k where m is the mass of the hydrogen atom and k the Boltzmann constant.

EXPERIMENTAL PROCEDURE

A SHEET of platinum was placed between two heavy steel tubes with integral flanged ends ground flat and smooth and put under pressure by means of bolts through heavy steel rings on either side of the flanges. It was not found necessary to make grooves in the ground ends in order to prevent leakage.

A moderate vacuum of about 10^{-2} cm Hg was maintained on one side and H_2 at atmospheric pressure allowed to flow to the other side, the excess burning in a small flame kept at constant height.

Rates were measured both with McLeod gauges of quite different volumes and also by a manometer, the scheme being quite similar to that used by Richardson, Nicol and Parnell,[1] with the minor addition of a tungsten point inserted in one arm of the manometer about 2 mm above the mercury level and connecting with a neon lamp. These arrangements are shown schematically in Fig. 1.

The steel tubes with a sheet of the material to be tested between were placed in a resistance furnace with Chromel Alumel thermocouples in contact (a) with the sheet on the H_2 side, (b) with the steel container outside the platinum and (c) about half way along the tubes and (d) next the water cooler as shown in the diagram. The temperatures indicated by (a), (b) and (c) couples were nearly the same and could be kept sufficiently constant without difficulty. The area of a sheet exposed to H_2 was very sharply defined by the marks of the steel holder. The rates were computed in the usual way by measuring rate of change of pressure in a given time for a known volume, and also by using a neon lamp arrangement by measuring the times for a given change of pressure also for a known volume.

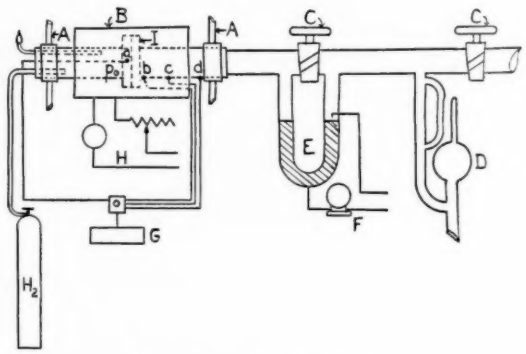

FIG. 1. Diagram of apparatus.

a, *b*, *c* and *d*, thermocouples
A, water coolers
B, electric furnace
C, stopcocks
D, McLeod gauge
E, mercury manometer
F, neon light circuit
H, heater circuit
I, adaptor
G, potentiometer
H_2, commercial tank hydrogen
p_0, pressure ingoing surface

It is desirable to keep the pressure low on the outgoing side, otherwise the sorption of the inside surface of the steel exit tube will diminish the

[1] O. W. Richardson, J. Nicol and T. Parnell, Phil. Mag. **8**, 1–29 (1904).

measured rate. Plating the inside of this part of the apparatus with gold would have avoided error from this source, since tests made with gold sheets in this same apparatus show that the transmission of hydrogen through gold over the range of temperatures used is undetectable.

After sufficient data had been obtained on Pt, a Ni disk was substituted for it and the work repeated. This nickel, not supposed to be particularly pure, contained 2.5 percent Fe by analysis and was from the G. E. Company.

A disk of platinum, supposedly pure as furnished by Baker and Company, was then placed in contact with a disk of the above mentioned nickel in the holders, the platinum being on the high pressure side, with the expectation that when heated the sheets would weld together, which was found to be the case; the runs were repeated with this double layer, the direction of flow then reversed and the observations taken again.

It is to be noted that with a large McLeod gauge no corrections for heated gas are necessary in computing rates, and with the small McLeod gauge such corrections are trivial, but with the manometer, which was found convenient, at the higher temperatures, a small correction was made following usual lines for the heated gas in that

TABLE I. *Observed rate of diffusion of hydrogen through Ni, Pt-Ni, Ni-Pt, and Pt.*

(a)		(b)		(c)		(d)	
Nickel		*Platinum-Nickel*		*Nickel-Platinum*		*Platinum*	
Area 3.6 sq. cm		Area 3.14 sq. cm		Area 3.14 sq. cm			
Thickness 0.0127 cm		Thickness		Thickness		Area 3.14 sq. cm	
Volume system 50 cc		Pt = 0.0102 cm		Ni = 0.0133 cm		Thickness 0.0133 cm	
		Ni = 0.0133 cm		Pt = 0.0102 cm		Volume system 237 cc	
		Volume system 237 cc		Volume system 237 cc			
T°K	Rate μ/min.	T°K	Rate μ/min.	T°K	Rate μ/min.	T°K	Rate μ/min.
649	244	620	8.5	711	5.25	705	3.95
664	309	633	8.4	753	10.5	720	5.5
718	590	634	8.2	769	13.2	723	5.8
737	807	667	18.0	770	14.0	725	5.9
788	1310	689	28.3	827	29.6	746	8.35
829	2380	690	28.0	888	66.8	754	9.9
855	2800	704	30.0	829	32.0	755	9.85
873	3410	707	26.5			757	10.75
		751	49.5			781	14.7
		799	82.3			802	20.7
		803	82.6			807	21.3
		841	134.0			827	30.0
		853	158.0				
Slope		Slope		Slope		Slope	
$b_1 = 6700 \pm 100$		$b_1 = 6690 \pm 40$		$b_1 = 9005 \pm 30$		$b_1 = 9000 \pm 40$	

Slopes are given for these data substituted in the equation $R = Ae^{-b_1/T}$.
Rate (R) is expressed in change of pressure in microns per minute for the particular volume of the system used.

TABLE II. *Computed rate of diffusion of hydrogen through Ni, Pt-Ni, Ni-Pt, and Pt on the assumption that slopes in Fig. 2 of Ni and Pt-Ni, also Pt and Ni-Pt are identical.*

Temp.	Nickel	Platinum-Nickel	Nickel-Platinum	Platinum
600°	303×10^{-11} g/cm² sec.	74.8×10^{-11}	6.8×10^{-11}	6.36×10^{-11}
700°	1484×10^{-11}	367×10^{-11}	58.1×10^{-11}	54.3×10^{-11}
800°	4890×10^{-11}	1209×10^{-11}	290×10^{-11}	271×10^{-11}
Slope	6690°	6690°	9005°	9905°

A conservative estimate of the relative consistency of the values of these slopes is P.E. = ±100 for all.

The rates above are in grams per sec. per sq. cm for the particular thicknesses used. Said thicknesses may be found at the top of Table I.

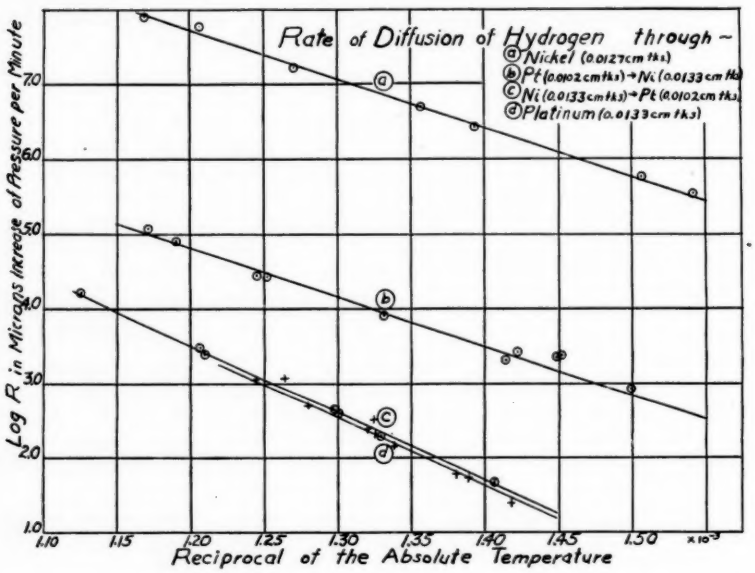

FIG. 2. Observed rate of diffusion of hydrogen through Ni, Pt-Ni, Ni-Pt and Pt

part of the apparatus in the furnace.

Four original sets of data including all rates as taken are given in Table I, a, b, c, and d and shown graphically on Fig. 2 which fits Table I. All the slopes in Fig. 2 were computed by least square methods, the lines drawn and the points then inserted. Table II shows results for 600 and 700°K computed on the basis of the experimental rates at 800°K and on the assumption that the b values for Ni and Pt-Ni are identical and also that the b of Pt and Ni-Pt is the same. Table II is inserted for use in calculations in order to avoid experimental errors as far as possible.

Discussion of Results

It is immediately apparent that the work of Borelius[2] and others is checked quite completely for single sheets, but the data on double layers make it clear that the emergent surface is the controlling factor so far as the temperature coefficient of the rate is concerned, since the curve of hydrogen through Pt-Ni is parallel to the curve of hydrogen through Ni and the hydrogen through Ni-Pt curve is parallel to the hydrogen through Pt curve.

[2] Borelius and Sven Lindblom, Ann. d. Physik **82**, 201 (1927).

Theory

Since the results of the experiments on double layers of nickel and platinum emphasize the importance of the outgoing surface, in discussing the theory of the passage of gas through a sheet of metal, it seems reasonable to ascertain whether the simple kinetic theory of flow through a surface does or does not apply. In the following Eqs. (1), (2) and (3), the symbols are defined as follows:

dm/dt = rate of diffusion of hydrogen in g cm^{-2} sec.$^{-1}$
p_t = pressure, in dynes, of hydrogen just inside the outgoing surface
m = mass in grams of hydrogen ion (or atom)
k = Boltzmann constant
T = absolute temperature
b_2 = surface work function expressed in equivalent degrees
p_0 = impressed pressure
A = a constant characteristic of material
x = thickness
b_1 = net apparent work function for flow, often erroneously associated with heat of dissociation, but really the sum of two work functions (as later appears).

Kinetic theory gives for flow of hydrogen through a surface,

$$dm/dt = p_i \cdot (m/2\pi k)^{\frac{1}{2}} \cdot T^{-\frac{1}{2}} \cdot \epsilon^{-b_2/T}. \quad (1)$$

But this same rate of flow of hydrogen through a metal sheet is empirically,

$$dm/dt = A(p_0^{\frac{1}{2}} - p_i^{\frac{1}{2}})/x \cdot \epsilon^{-b_1/T} \quad (2)$$

as given by Borelius,[2] who seems the most careful of recent investigators and who has thus modified the original equation of Richardson[1]; e.g.,

$$dm/dt = A \cdot (p_0^{\frac{1}{2}}/x) \cdot \epsilon^{-b_1/T} \quad (3)$$

by the subtraction of the quantity $p_i^{\frac{1}{2}}$ from the square root of the impressed pressure. He does this because, in plotting rate of flow dm/dt against the square root of the impressed pressure ($p_0^{\frac{1}{2}}$), he finds for any particular temperature an approximately linear relation between the impressed pressure and the rate of flow, that is, for the larger pressures. When this straight line is extended to the $p_0^{\frac{1}{2}}$-axis, it does not pass through the origin, but has a $p_0^{\frac{1}{2}}$ intercept which he calls p_i. We wish to define further this quantity, p_i, by association with the pressure p that appears in the kinetic theory. Eq. (1).

However, before we substitute numerical data we must introduce a relation (which also may be regarded for the present as empirical) between p_i, the equivalent inside pressure on the outgoing side, and p_1 the corresponding pressure on the ingoing side. This is necessary in order to derive and extend Borelius' (or Richardson's) empirical flow equation from the flow equation of the kinetic theory. Such an empirical relation may be written as follows:

$$p_i = p_1(1 - \epsilon^{-a/x}). \quad (4)$$

If we assume equilibrium to be reached in the reaction represented by $\frac{1}{2}H_2 \leftrightarrow H^+ + e^-$ at the ingoing side we may write $p_1^2/p_0 = M$ and the equation becomes

$$p_i = M p_0^{\frac{1}{2}}(1 - \epsilon^{-a/x}),$$

and since

$$M = M_0 \epsilon^{-\Delta w/T}$$

(derivable from fundamental thermodynamics)

$$p_i = M_0 \epsilon^{-\Delta w/T} \cdot p_0^{\frac{1}{2}} \cdot (1 - \epsilon^{-a/x}),$$

where the quantities involved are

p_0 = impressed pressure
a = a constant of the material
x = thickness
M_0 = mass action constant
Δw = the heat of solution per gram atom divided by R
T = absolute temperature.

Substituting (4) in (1) gives

$$\frac{dm}{dt} = aM_0\left(\frac{m}{2\pi k}\right)^{\frac{1}{2}} \cdot \frac{p_0^{\frac{1}{2}} - p_0^{\frac{1}{2}}(a/2x)}{x} \cdot T^{-\frac{1}{2}} \cdot \frac{-b_2 - \Delta w}{T}$$
$$= A\left(\frac{p_0^{\frac{1}{2}} - p_i^{\frac{1}{2}}}{x}\right) \cdot T^{-\frac{1}{2}} \cdot \epsilon^{-b_1/T} \quad (5)$$

this latter being identical with the Borelius (or Richardson) formula except for the $T^{-\frac{1}{2}}$ which could not have been detected.

We shall, therefore, introduce this $T^{-\frac{1}{2}}$ in both Richardson's and Borelius' equations for handling numerical data.

Since p_i in general is small compared with p_0, to a close approximation Eq. (5) may be written

$$dm/dt = (A p_0^{\frac{1}{2}}/x) \cdot T^{-\frac{1}{2}} \cdot \epsilon^{(-b_2 - \Delta w)/T}. \quad (6)$$

And comparing with Eq. (1) and solving for P_i,

$$p_i = A p_0^{\frac{1}{2}}/x(2\pi k/m)^{\frac{1}{2}} \cdot \epsilon^{-\Delta w/T}. \quad (7)$$

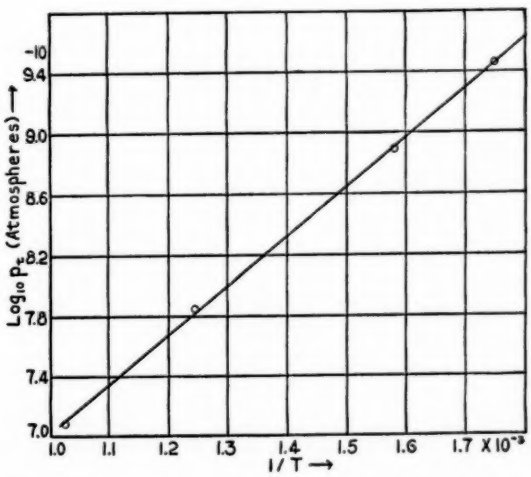

FIG. 3. Relation between back pressure in iron (p_i') and absolute temperature (T) from Table III. (Data of Borelius and Lindblom.)

Taking logs for a case where p_0 and x is constant

$$\log p_t = \log (\text{const.}) - \Delta w/T.$$

Borelius' data for p_t and T are tabulated in Table III which also includes p_t' found as indicated in footnote of tabulation and involving a small graphic correction, chiefly of theoretical importance. The relation between p_t' and T is shown graphically in Fig. 3. We note from the slope that $\Delta w = 7500°$ approximately, and is positive, hence may be associated with energy released.

TABLE III. *Data of Borelius and Lindblom on internal pressures in iron at various temperatures with calculated values of $(m/k)^{\frac{1}{2}}$ and calculated internal pressure from kinetic theory equation of flow.*

	From Borelius Data			*Calculated*	
(a)	(b)	(c)	(d)	(e)	(f)
$T°K$	$dm/dt \times 10^9$ g/sec.	p_t (atmos.)	p_t' (atmos.) (corrected)	p_t calculated (atmos.)	$(m/k)^{\frac{1}{2}}$
975	3.	0.0012	0.0012	0.001	0.9×10^{-4}
805	1.	.007	.007	.005	$.8 \times 10^{-4}$
633	0.2	.07	.08	.06	$.7 \times 10^{-4}$
571	0.09	.25	.30	.23	$.8 \times 10^{-4}$

Accepted Values

$m_H = 1.66 \times 10^{-24}$ grams $\qquad (m/k)^{\frac{1}{2}} = 1.09 \times 10^{-4}$

$k = 1.372 \times 10^{-16}$ ergs/degree

Final value of work function at outgoing surface for hydrogen through iron; $-b_2 = 5200° + 7500° = 12{,}700°$.

Note: p_t' differs from p_t in that it is taken from the $p_0^{\frac{1}{2}}$ intercept of the tangent to Borelius curves at the tabulated values of dm/dt instead of from the $p_0^{\frac{1}{2}}$ intercept of the lines drawn as in Borelius' paper.

Using Eq. (5) and Borelius' data for the same iron, we find $b_2 + \Delta w = -5200°$ approximately.

Hence b_2, which may be defined as the work function at the back surface from the kinetic theory, (Eq. (1)), is given by

$$b_2 = -5200° - 7500° = -12{,}700°.$$

Having found this back surface work function we may test Eq. (1) directly by substitution of numerical values. The author has chosen to regard $(m/k)^{\frac{1}{2}}$ as the unknown. The various values of $(m/k)^{\frac{1}{2}}$ thus obtained as shown in Table III and are of the same order of magnitude as found in any handbook that has universal physical constants. The variation does not seem beyond experimental error.

This seems very significant, since, considering the magnitude of the various quantities involved, the chance for such a check being accidental is very remote.

To summarize: The application of two principles and one empirical relation seems to give the equation of flow of hydrogen through Fe, Ni, and Pt; these are:

(a) A mass action formula associated with a reaction

$$\tfrac{1}{2}H_2 \leftrightarrow H^+ + e^-.$$

(b) An empirical relation between inside pressure of hydrogen (or concentration) at back surface and inside pressure at front surface, previously given as (Eq. (4)).

(c) The kinetic theory equation for flow of a gas across a potential barrier.

That is, starting with (c) substituting (b) and then (a) gives a form of Richardson's equation; namely,

$$dm/dt = (A p_0^{\frac{1}{2}}/x) \cdot T^{-\frac{1}{2}} \cdot \epsilon^{-b_1/T}.$$

Direct experiments on double layers of platinum and nickel show that the temperature coefficient of flow is *wholly dependent on the outgoing surface*, as would follow from (a), (b) and (c), and in general with metals behaving as do platinum, nickel and iron toward hydrogen, the *exit surface* largely determines the rate of diffusion, at least for such temperatures as are usually employed in diffusion experiments.

Note: Equations of flow of hydrogen through Ni and Pt and through double layers of these two metals are also sufficient for an approximate determination of $(m/k)^{\frac{1}{2}}$. Solution of such simultaneous equations takes much space and, therefore, has not been included. In both methods of approach one would expect a variation with temperature of the viscosity coefficient (associated with "a" of Eq. (4)); apparently the effect is small since the computed values of $(m/k)^{\frac{1}{2}}$ from either method are not much more different from accepted values than could be attributed to experimental error.

The experimental work connected with this

paper has largely been done by Mr. J. D. Sauter and assistants, and much aid in the calculations has been furnished by Messrs. M. A. Jeppesen and K. D. Larsen, all of the Physics Department of The Pennsylvania State College. Suggestions have also been offered by Dr. E. P. Barrett of the School of Mineral Industries, and by Dr. W. P. Davey and Dr. J. G. Aston of the School of Chemistry and Physics of The Pennsylvania State College.

The Decomposition of Sodium Azide by Controlled Electron Bombardment and by Ultraviolet Light[1, 2]

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(Received March 22, 1933)

The decomposition of crystalline sodium azide has been brought about by bombardment with 11.65±0.2 volt electrons. The material to be decomposed was placed on the plate of a specially designed three electrode vacuum tube and the decomposition rate studied as a function of the voltage of the bombarding electrons. All decomposition rates were determined by the pressure change as measured on an ionization manometer, sodium azide decomposing into pure sodium and nitrogen. Periodic discontinuities in pressure were observed which are associated with the ionization manometer and the crystalline sodium azide. Solid sodium azide has been found to be decomposed photochemically by wave-lengths below approximately 405 $m\mu$. The rate of decomposition was directly proportional to the light intensity. There is no apparent relation between energies necessary for the electronic and photochemical decomposition.

INTRODUCTION

PRACTICALLY the first direct experimental proof of the validity of Bohr's stationary states was given by Franck and Hertz's critical impact measurements. The existence of definite energy levels within atomic configurations was established in that it was shown that electrons having definite velocities can experience inelastic encounters with atoms or molecules resulting in an exchange of energy. During the nineteen years that have elapsed since these epoch making experiments, physics and chemistry have been enormously enriched by the information yielded from such studies.

The synthesis of NH_3 and NO_2 by bombardment of a mixture of their constituents with low voltage electrons has been studied by several investigators. (See page 488.) These studies indicate clearly that synthesis and increase in reaction rate are closely related to the potentials at which the different atomic and molecular species arise.

The application of critical impact methods to the solid state has been fruitful in certain purely physical phenomena. In the emission of x-rays by metals, the Einstein equation for the inverse photoelectric effect holds very precisely. In the beautiful experiments of Davisson and Germer on the reflection of electrons from metals, a knowledge of the velocity of the electrons and the arrangement of atoms in the crystal lattices suffice to confirm the de Broglie wave equation.

Although the extension of these methods to the chemical decomposition of solids appears very inviting and interesting, it is apparent at once that certain difficulties of procedure and indeed of interpretation will be met. Meiler and Noyes[3] have made just such a study on potassium chlorate. The evidence is that there is a slight decomposition produced by 22 volt-electrons. Noyes and Vaughan[4] in studying oxalic acid report decomposition with 4.5–5.5 volt-electrons.

Sodium azide was chosen for this work because it is a comparatively simple molecule; it has been shown to decompose smoothly into pure N_2 and Na, and should give no particular trouble with the use of filament sources of electrons. Under a wide range of conditions it was shown to yield a reproducible threshold value for decomposition.

EXPERIMENTAL

Vacuum system

A vacuum system of the usual type was employed, which is illustrated diagrammatically in

[1] Constructed from the thesis submitted by G. Calvin Brous in partial fulfillment of the requirements for the degree of Doctor of Philosophy in New York University, June, 1932.

[2] Presented before the division of Physical and Inorganic Chemistry of the 85th meeting of the American Chemical Society in Washington, D. C., March 28, 1933.

[3] Meiler and Noyes, J. Am. Chem. Soc. **52**, 527 (1930).

[4] Unpublished. Reported in Chem. Rev. **7**, 239–58 (1930).

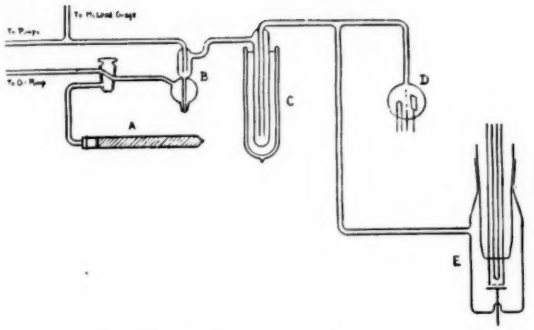

FIG. 1. Vacuum system. *A*, drying tube; *B*, mercury cut-off; *C*, liquid air trap; *D*, ionization manometer; *E*, reaction vessel.

Fig. 1. The pumps could be separated from the reaction end of the system by means of a mercury cut-off. The system was baked and the pumps operated until a pressure of 10^{-5} mm could be maintained for twenty-four hours, with the reaction end separated from the pumps.

In the preliminary work all pressures were tried. When using pressures of 10^{-6} to 10^{-5} mm, the clean-up was so great that the initial voltage at which decomposition occurred was never observed. At pressures higher than 5×10^{-4} mm, the filament did not function as efficiently as at lower pressures, neither were the reaction rates as continuous as they were when pressures of 10^{-5} mm were employed. In attaining a pressure of 10^{-6} mm, two liquid air cooled mercury vapor traps were employed and the system was baked for a period of 48 hours previous to separating the reaction end.

Reaction tube

Description of tube. The reaction vessel is illustrated in *E* of Fig. 1. It was 7.5 cm in diameter and 19 cm high. The in-seals were of tungsten and the electrodes were entirely of nickel.

In the first series of experiments, the filament was an oxide coated spiral 4 mm in diameter, the axis of which was parallel to the grid. The grid was of nickel gauze and placed 2 cm directly below the filament. The plate, 4 cm in diameter, was 2 mm below the grid. In these first experiments, the distance filament to plate was not decreased because it was feared that some thermal decomposition would result. As shown later, this precaution was needless.

In later experiments, a commercial filament of the type used in a 280 vacuum tube was employed. A strip 10 cm in length was placed in staggered form in a plane 0.5 cm above the grid. The grid was quite open and 1.5 mm above the plate.

The tube was so designed that the grid and filament were removable by means of a ground glass joint. The plate, being threaded, could be raised, lowered, or even removed. In determining the reaction rates of group III, a tube of slightly different design was used. In this tube the plate was a nickel gauze on which the sodium azide was deposited by evaporation from an aqueous solution. The electrode distances were of the same order as those used in determining the rates of group II.

Only filaments of the oxide type were used. Activation was secured in the usual manner through positive ion bombardment.

The arrangement of electrodes and the choice of grid for the first series of experiments were such as to give a definiteness of electron velocity at the expense of plate current. In the later determinations, the open grid and large filament gave high plate currents with a greater distribution of electron velocities.

Reaction tube circuit. To initiate the decomposition of the sodium azide, a special three electrode vacuum tube was used (Fig. 2). The return of the grid and plate circuit to the filament was made to the center of a 3000 ohm resistance shunted across the filament. This was done so that the potentials would be measured with reference to the electrical center of the filament. The electrons were accelerated with definite

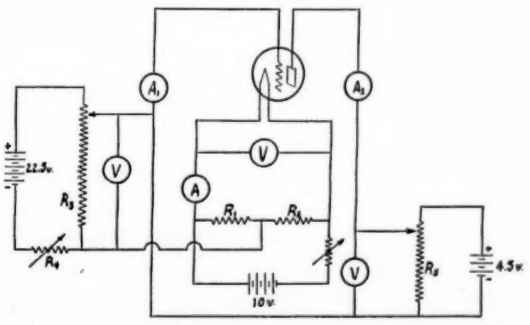

FIG. 2. Reaction tube circuit. R_1, R_2 : 1500Ω; R_3 : 3230Ω; R_4 : 400Ω; R_5 : 1500Ω; A_1 : 0–1.0 milliammeter; A_2 : 0–200 microammeter.

velocities by the grid, and the plate was kept ½ volt positive at all times with respect to the grid. The latter was done to aid in the removal of any charge which might build up on the plate, because of its being covered with a nonconductor.

The filament temperature was kept constant throughout each determination, the current being secured from a bank of storage batteries. The filament usually required a current of 2.25 amperes at 6 volts.

Adjustment of both accelerating potentials was maintained by use of voltage dividers across the grid and plate circuit batteries. A variable resistance (R_4) was introduced to give greater control of the grid potential. A 0–200 microammeter was used to measure the plate current at the lower voltages.

Recording system

At all times the rates of reaction were determined by the change of pressure as measured on an ionization manometer of the Buckley type. In the reactions of group I the manometer was operated directly from the 110 volt d.c. line. In Fig. 3 is shown diagrammatically the circuit as

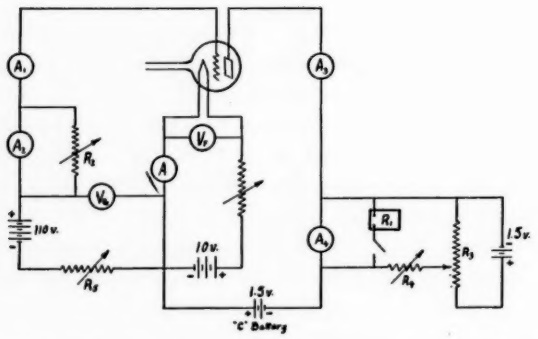

FIG. 3. Ionization manometer circuit. R_1, R_2 : decade boxes; R_3 : 30,000Ω potentiometer; R^4 : 15,300Ω; R_5 : 1900; A_1 : 0–100 milliammeter; A_2 : 0–1.5 milliammeter; A_3 : 0–15 microammeter; A_4 : 0–0.5 microammeter.

used in the determinations of the rates in groups II and III.

The filament was kept at a dull red heat and its temperature constantly adjusted to maintain a grid current of 10 milliamperes, for data in group II, and 20 milliamperes for data in group III. The grid was maintained at 110 volts positive with respect to the negative side of the filament, a bank of storage batteries being the source of potential.

By means of the "C" battery the plate was kept 1.5 volts negative with respect to the negative side of the filament. By using the null method shown in the plate circuit of Fig. 3, it was possible to measure absolutely any increase in positive ion current resulting from the decomposition of the sodium azide.

When the grid current is 20 milliamperes, a positive ion current of 1 microampere corresponds to a pressure of 5×10^{-6} mm. The best rates were obtained at pressures of 10^{-4} to 10^{-5} mm.

Control refinements

Even with the elaborate control just described, discontinuities in rate curves would arise. Control of liquid air level to ±1.5 mm improved conditions but still discontinuities occurred.

Since the grid current varied with change in pressure, controls for the grid current of the ionization manometer were devised.

The first attempt was to control the grid current by limiting it to the saturation current of a UX-210 radio tube, in which the grid and plate were shorted, and the tube operating as a diode. This method gave some control but only at the expense of the grid current in the ionization manometer.

A grid bias method of control similar to the automatic volume control used in broadcast receivers was then tried. The same objection applied to the use of this circuit.

It was then decided to build a thermostat about the ionization manometer and the reaction tube. That discontinuities would arise due to temperature changes about the apparatus, could be easily demonstrated. Momentary fanning of the system would immediately produce a small drop in pressure.

The thermostat was designed to keep the tubes at a temperature of 31±0.05°C. The heating unit was a 50 watt light bulb. The thermal control was obtained by using a long glass tube filled with toluene which terminated in a mercury filled capillary. The actual regulation was secured through vacuum tube thermostat control as developed by Beaver.[5]

[5] D. J. and J. J. Beaver, Ind. Eng. Chem. **15**, 359 (1923).

However, it must be emphasized here that regardless of the control refinements used, they served only to define more clearly the fact that periodic variations in pressure were occurring which were entirely independent of external factors. With this understood, no automatic regulation was employed; however the thermostat was left about the tubes to protect them from drafts and sudden changes in temperature.

Procedure

Preliminary work

Purification of sodium azide. For the first experiments, the sodium azide was recrystallized three times from a water and alcohol solution, after which it was dried for several hours at 120°C and kept in a desiccator over P_2O_5 for a week. In the later experiments Kahlbaum's C.P. sodium azide was used without further purification.

Preparation of reaction system. The sodium azide was placed in a very thin layer on the plate of the reaction tube. The ground glass joint supporting the filament and grid was then sealed in with hard de Khotinsky cement and the system degassed using electric heaters until a pressure of less than 10^{-5} mm could be maintained. The filaments were activated and maintained at operating temperature for half an hour before the reaction end of the system was separated from the pumps.

Decomposition at high voltages. Bombarding the sodium azide for a short time with 35 volt-electrons, sufficed to show that decomposition was taking place. If the potential were raised to above 50 volts, decomposition was so rapid that in a very short time the characteristic blue glow of nitrogen would appear.

Investigation for thermal decomposition. Knowing that decomposition actually occurred, it was desirable to determine if there were any thermal reaction. No decomposition was evident over a period of $1\frac{1}{2}$ hours when the filament was brightly lit and no accelerating voltage applied. In fact, no decomposition was ever observed at any potential up to 11.5 volts.

Investigation of vapor pressure of sodium azide. Sodium azide was also shown to have a negligible vapor pressure; impacts in the gas phase would thus be absent. The degree of vacuum obtainable was limited only by the extent to which the system was degassed.

Rate determinations

Reaction rates for each voltage were calculated from pressure readings taken at 5-minute intervals over a period of one hour. During the last hour of the degassing of the system, the filaments were kept lighted. The high vacuum end of the system was then separated from the pumps by means of the mercury cut-off. Before the accelerating voltage was applied, pressure readings were taken over a period of 15 minutes to insure that the system was in a state of equilibrium. On applying the accelerating potential, there was always a sudden rush of gas after which the rate became constant.

Critical potential measurements were made in order to prove the gas to be nitrogen and to calibrate the tube for contact potentials.

Data

In the electronic decomposition the data are divided into three main groups. Group I contains the reaction rates and calibration data determined with the oxide coated spiral filament and small mesh grid. Group II contains the results obtained with the oxide ribbon filament and the open grid together with the data for its calibration. Group III records the data for rates at the higher voltages. In this case an aqueous solution of sodium azide was evaporated on a fine mesh gauze. Each group represents the data taken under nearly identical conditions of tube design.

The rate of reaction is indicated by the slope of the pressure-time curve. The rate (S) is calculated from $(dI^+/dt)60$, where I^+ is the positive ion current and t is time in minutes. Absolute rates are determined from S/I_p, which is the rate per unit electron current.

Group I

In all the following data in groups I, II and III, (Table I) V_p and V_g the plate and grid potentials, are measured in volts. The values of I_p and I_g, the plate and grid currents, are recorded in milliamperes, and the positive ion current is recorded in microamperes. Time is in minutes.

TABLE I. *Tabulation of reaction rates for group I.*

Rate No.	V_p	S in Microamperes hour	I_p	Slope/I_p
1	00.5	0	0	0
2	05.5	0	0.007	0
3	10.5	0	.063	0
4	11.5	0	.091	0
5	12.5	0.025	.097	0.26
6	13.5	.11	.115	0.96
7	14.5	.238	.142	1.67
8	15.5	.160	.132	1.21
9	16.5	.280	.105	2.67
10	17.5	.50	.172	2.91
11	18.5	.64	.190	3.37
12	19.5	.82	.210	3.90
13	20.5	1.05	.220	4.71

Fig. 4 is a plot of the rate per unit electron current (Slope/I_p) as a function of the electron voltage.

In the first four rates at plate potentials of 0.5, 5.5, 10.5 and 11.5 volts, no decomposition was discernible. In Rate No. 1, the change in positive ion current was ± 0.05 microampere over a period of three hours. Rate No. 4 was equally as constant and was observed over a period of $1\frac{1}{2}$ hours. Rates No. 5 and above, all showed a distinct increase of pressure with time.

Critical potential measurements to calibrate the tube for contact potentials indicated the species N_2^+ to occur at 17 volts. (Tube I.) (Table II.)

TABLE II. *Tabulation of reaction rates for group II.*

Rate No.	V_p	S in Microamperes hour	I_p	Slope/I_p
1	0	0.012±.02	0.00	—
2	12	.033±.10	.051	0.65±1.95
3	12.5	.116±.012	.058	2.00±0.20
4	13.5	.197±.011	.070	2.81±0.15
5	14.5	.214±.011	.084	2.55±0.13
6	15.5	.364±.016	.098	3.71±0.17
7	16	.011±.002	.107	0.11±0.02
8	16.5	.678±.022	.116	5.84±0.19
9	17	.876±.012	.133	6.59±0.09
10	12	.047	.055	0.86±0.53
11	12.25	.036	.052	0.70
12	11.75	.00	.046	0.00
13	13	.160	.066	2.50
14	14	.300	.080	3.705
15	15	.00	.095	0.00
16	15.5	.00	.102	0.00
17	16.25	.276	.114	2.421
18	14.5	.726	.216	3.36
19	13.5	.744	.225	3.30

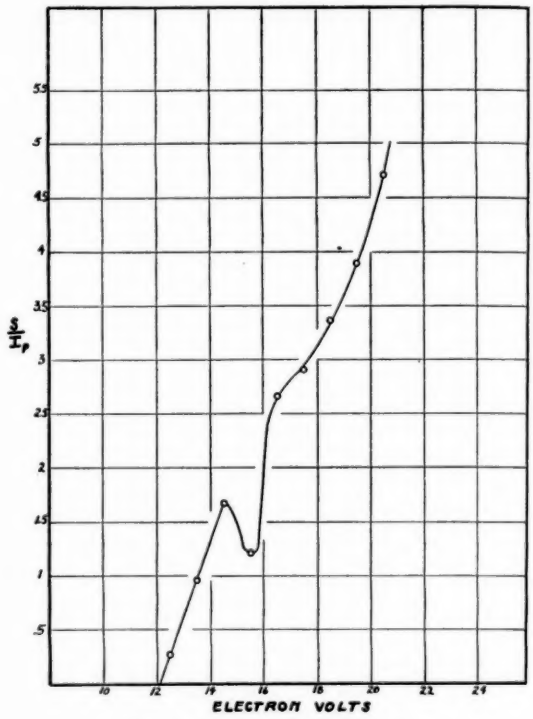

FIG. 4. Reaction rates, tube I.

GROUP II

In Fig. 5, the individual rates per unit electron current (S/I_p) are plotted as a function of the voltage of bombarding electrons.

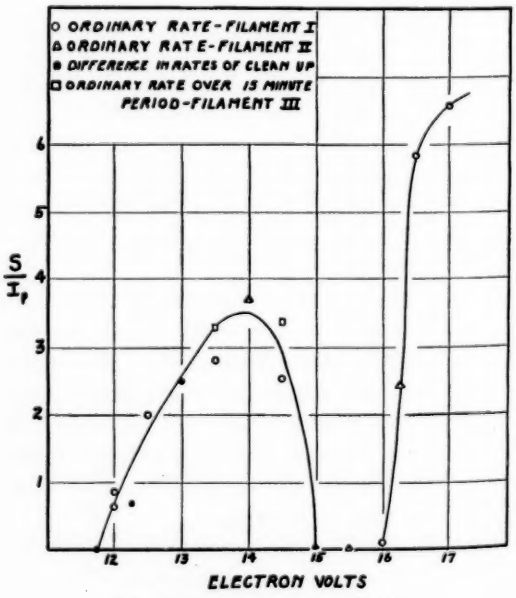
○ ORDINARY RATE-FILAMENT I
△ ORDINARY RATE-FILAMENT II
● DIFFERENCE IN RATES OF CLEAN UP
□ ORDINARY RATE OVER 15 MINUTE PERIOD-FILAMENT III
S/Ip
ELECTRON VOLTS

FIG. 5. Reaction rates, tube II.

Note: Rate No. 6 appears to be anomalous and so is not included in Fig. 5. The values of S in Rates Nos. 1–10 were determined by the method of least squares. These values sufficed to show that graphic determination of S was equally as satisfactory as determination through the method of least squares. The graphic method was used on all other rates in groups I, II and III.

The complete data for the individual rate No. 8 are included in Table III to illustrate the manner in which the data were taken.

TABLE III. *Rate No. 8.*

Filament 2.5 amperes, 7.0 volts. Buckley gauge: I_F = 1.4 amperes; V_F = 4.2 volts; V_g = 110 volts; I_g = 10 milliamperes

Time	V_g	I_g	V_p	I_p	Microamperes
0	16	0.29	16.5	0.115	5.80
5					5.97
10					5.97
15				0.116	6.02
20					6.08
25					6.20
30					6.20
35					6.26
40					6.35
45					6.37
50					6.40
55					6.50

$S = 0.678 \pm 0.022$ Error = 3.20% as calculated by method of least squares

$S/I_p = 0.678 = 5.84 \pm 0.19$

0.116

Average deviation of I^+ calculated, from I^+ observed $= \pm 0.017$.

S is recorded in microamperes per hour.

Critical potential measurements again served to identify the reaction product as nitrogen, N_2^+ appearing at 16.8 volts. Some of the sodium azide was then decomposed thermally to permit measurements at a higher pressure. Four of the critical potentials of nitrogen were observed.

GROUP III

The data below (Table IV) are recorded graphically in Fig. 6. Curve I is a record of determinations made either at very low pressures or with the pressure increasing as the plate voltage increased. For the data as recorded in curve II, the electron voltage was decreased as the pressure increased. A possible explanation of these negative rates will be discussed later.

TABLE IV. *Tabulation of reaction rates for group III.*

Rate No.	V_p	S in Microamperes per hour	I_p	S/I_p
A. Voltage increasing as pressure increases (curve I, Fig. 6)				
1	20.5	1.50	0.090	16.7
2	21.5	5.10	.09	56.7
3	22.5	6.42	.12	53.5
4	23.0	1.95	.135	14.5
5	23.5	2.48	.154	16.1
6	25.5	14.10	.153	92.2
7	25.0	6.43	.158	40.7
8	24.75	6.80	.170	40.0
9	26.5	22.8	.208	109.6
10	27.0	27.6	.206	138.8
11	27.5	15.2	.222	68.5
12	28.0	12.8	.242	52.9
B. Voltage decreasing as pressure increases (curve II, Fig. 6)				
13	28.0	16.9	0.237	71.2
14	27.5	7.4	.227	32.6
15	27.0	9.2	.228	40.4
16	26.5	3.0	.220	13.6
17	26.0	−0.90	.213	− 4.2
18	25.0	−3.30	.20	−16.5
19	24.0	−6.80	.183	−37.2
20	22.0	−7.40	.142	−52.1

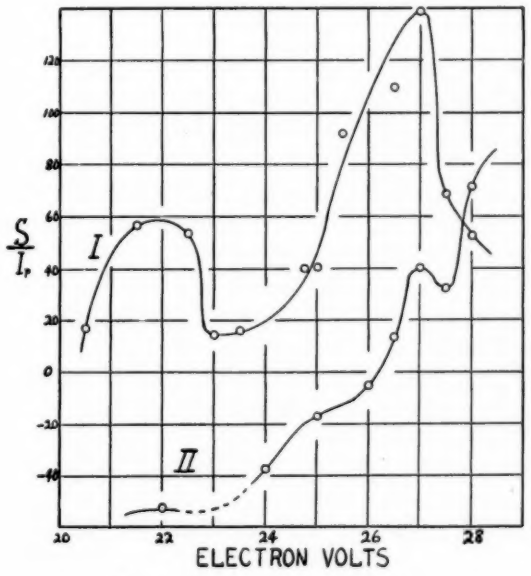

FIG. 6. Reaction rates, tube III.

Reaction rate as a function of accelerating potential

All reaction rates were determined as the change in positive ion current per hour per unit plate current in the reaction tube. Plates 1, 2 and 3 are a plot of rate per unit plate current as a function of the electron voltage. The first two of

these figures suffice to show that the threshold potential for decomposition is at or very near 12 volts. Group I would place this value at 12.1 volts, while group II would indicate 11.8 volts, both values being uncorrected for contact potentials. No decomposition was ever observed with 11.75 volt-electrons (uncorrected).

Above 12 volts the reaction rate increases rapidly, showing distinct minima at 15.5 volts, 23.5 to 24.0 volts, and 27.5 volts. That these values correspond to critical potentials for nitrogen is at once evident. The important fact is that they cannot be due to nitrogen in the gas phase. All decomposition rates were reduced to rates per unit electron current. If the electron current were lessened because of inelastic impacts with nitrogen molecules in the gas phase, reduction of all decomposition rates to rate per unit electron current would correct for this factor. The positive ion current at these pressures as recorded by the ionization manometer was negligible, being of the order of microamperes. Also, at pressures less than 10^{-4} mm the mean free path of electrons in nitrogen is at least 40 cm, which is 80 times the distance filament to plate. For this distance only 1 percent of the electrons undergo collision with a gas molecule before striking the plate. A reasonable explanation is that the decrease in decomposition rate is due to impact of the electrons with adsorbed nitrogen molecules on the surface of the sodium azide.

TABLE V.

	N_2^+	N^+
Vaughan[6]	15.8	24.5
Kallmann and Rosen[7, 8]	16.0	24.0
Hogness and Lunn[9]	17.0	24.0
Mackay[10]	16.3	
Smyth and Stueckelberg[11]	16.5	
Tate and Smith[12]	15.7	
Samson and Turner[13]	17.44 was the highest.	
Harnwell[14]		About 24 and definitely below 24.5.

[6] Vaughan, Phys. Rev. **38**, 1687–95 (1931).
[7] Kallmann and Rosen, Zeits. f. Physik **58**, 52–8 (1929).
[8] Kallmann and Rosen, Phys. Zeits. **30**, 772–3 (1929).
[9] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).
[10] Mackay, Phys. Rev. **24**, 319 (1924).
[11] Smyth and Stueckelberg, Phys. Rev. **36**, 478 (1930).
[12] Tate and Smith, Phys. Rev. **39**, 270–77 (1932).
[13] Samson and Turner, Phys. Rev. **34**, 747 (1929).
[14] Harnwell, Phys. Rev. **29**, 830 (1927).

Calibration of tube for contact potentials

There is considerable disagreement in the recorded values for the critical potentials for nitrogen. For the appearance of the species N_2^+, there is variation from 15.8 to 17.00 volts, while for the appearance of N^+, the values range from 24 to 24.5 volts.

In Table V are the values for these potentials as recorded by some of the later investigators.

In considering these different values and their methods of determination, Smyth[15] has selected 16.5 volts and 24 volts as the most probable potentials. The recent work of Tate and Smith[13] together with results of the above investigators indicates that 15.8 volts is probably more nearly the correct value for N_2^+.

Of significance are the critical potentials observed for rate increases in the synthesis of NH_3 and NO_2.

On reference to the works of authors in Table VI in the synthesis of NH_3, marked rate increases were found at those potentials corresponding to the appearance of N_2^+ and N^+.

TABLE VI.

	N_2^+	N^+
Andersen[16]	17 volts	
Storch and Olsen[17]		23 volts
Rideal and Caress[18]	17 volts	23 volts
Brett[19]	17 volts	24.5 volts

Likewise in the electronic synthesis of NO_2, the following potentials for rate increase were obtained.

	N_2^+	N^+
Wansbrough-Jones[20]	17 volts	23 volts
Henry[21]	16.8 volts	23.1 volts

[15] Smyth, Rev. Mod. Phys. **3**, 371 (1931).
[16] Andersen, Zeits. f. Physik **10**, 54–62 (1922).
[17] Storch and Olsen, J. Am. Chem. Soc. **45**, 1605 (1923).
[18] Caress and Rideal, Proc. Roy. Soc. (London) **A115**, 684–700 (1927).
[19] Brett, Proc. Roy. Soc. (London) **A129**, 319–27 (1930).
[20] Wansbrough-Jones, Proc. Roy. Soc. (London) **A127**, 511–29 (1930).
[21] Henry, Bull. soc. chim. Belg. **40**, 371–84 (1931); J. Phys. Chem. **34**, 2782–91 (1930).

TABLE VII. *Summary.*

Species	Nitrogen in gas phase		Minima in reaction rates		Best probable value from the literature
	Observed	Corrected	Observed	Corrected	
N_2^+	16.8 ±0.1	16.62±0.1	15.5 ±0.3	15.32±0.3	15.8
N^+	23.75± .1	23.57± .1	23.75± .5	23.57± .5	24.0
$N^{+\prime}$	27.4 ± .1	27.22± .1	27.5 ± .3	27.32± .3	

Correction for Tubes II and III — Contact potentials etc. = +0.18 volts
Correction for Tube I (N_2^+ at 17 volts) — Contact potentials etc. = +0.38 volts
Corrected critical potential for initial decomposition of sodium azide — Group I = 11.7 volts; Group II = 11.6 volts

Critical potential measurements on helium to calibrate the tube for contact potentials showed the species He^+ occurring at 24.65±0.1 volts. The spectroscopic value for He^+ is 24.47 volts. This would indicate that all observed potentials are 0.18±0.1 volt too high.

The above values in Table VII were recorded with rugged filaments which are necessary to deliver high emission for decomposing the sodium azide. One cannot expect these measurements of critical potentials to compare with the accuracy of positive ion determinations in which high resolution and very small currents are used. With the exception of the potential for N_2^+ in the gas phase, all observed potentials (corrected) are 0.4 to 0.5 volt lower than the most probable values observed by other investigators. It is evident from the recent work of Vaughan and of Tate and Smith that the value for this potential is 15.8 volts or slightly lower; our value for this potential, as well as the values obtained by previous investigators, is much higher.

"Clean-up" effects

Change of liquid-air level about the mercury vapor trap would produce a slight change of pressure. To eliminate this variation, the level was maintained constant to ±1.5 mm. There is always the clean-up due to evaporation of the filament. The filament was operated at a dull red heat. That some evaporation occurred was evident from the blackening of the tube near the filament.

Lighting a filament would cause a slight increase of pressure; this effect is purely thermal. The first application of the accelerating potential would bring about an increase in pressure, which probably is due to a degassing of the sodium azide surface, after which the rate of pressure-change would become constant.

Coincident with the above effects there undoubtedly exists a clean-up due to ionization. This will occur primarily because of the ionization manometer. Campbell and New[22] in a comprehensive investigation of this type of clean-up find the rate of gas disappearance per positive ion formed increases with rise of pressure, finally reaching a constant rate at higher pressures.

Periodic discontinuities in pressure

Interesting in this investigation was a periodic fluctuation in pressure. Abrupt pressure increases would occur in which the period between outbursts was as high as 45 minutes. (Rate 4, Fig. 7.) Rates 9, 10, 11, and 12, Fig. 7, illustrate the outbursts as they were occurring at another time for which the period was 28 minutes. Measurements showed that the time interval between jumps was constant to within one second. The ionization manometer was then sealed from the system so that it would operate alone at the same pressure as that at which the decomposition had occurred. The periodic jumps in pressure did not occur with the ionization manometer alone; however, they did occur when both tubes were connected to the vacuum line with only the ionization manometer operating.

The inference is that the periodic outbursts are associated in some manner with the crystalline sodium azide. One is reminded of the discontinuities in adsorption observed by Benton and White,[23] and Allmand, Burrage and Chaplin.[24, 25]

[22] N. R. Campbell and E. G. New, Phil. Mag. **48**, 560 (1924).

[23] Benton and White, J. Am. Chem. Soc. **53**, 2807 (1931).

[24] Burrage, J. Phys. Chem. **37**, 41 (1933).

[25] Allmand, Burrage and Chaplin, Trans. Faraday Soc. **28**, 218 (1932).

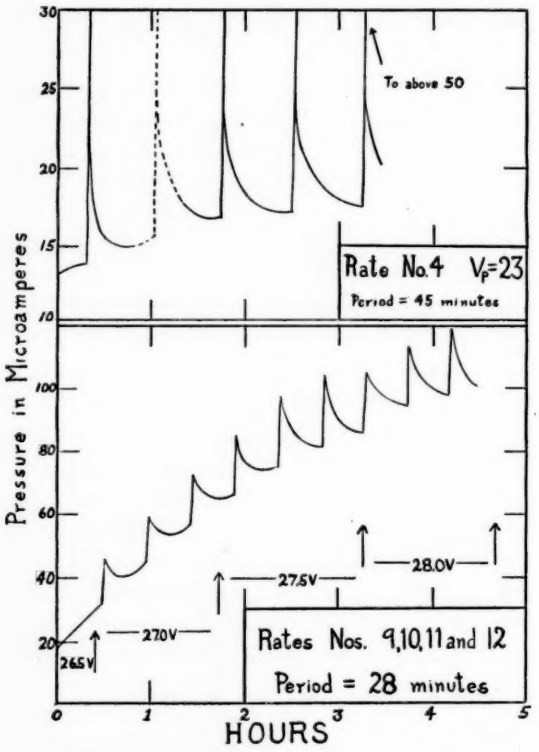

FIG. 7. Periodic discontinuities in decomposition rates.

It is certain that the time interval between jumps is dependent upon the gas in the system. Helium gave approximately half the period observed for nitrogen. The outbursts occurred in exactly the same manner whether the pressure in the system was increasing or decreasing.

It is these discontinuities for which the various methods of pressure control refinement were devised. These discontinuities are now being made the subject of a detailed investigation which will be reported in a later communication.

Reaction rates as a function of pressure

The rates as recorded in groups I and II, because of the small pressure change, were determined at practically the same pressure. For group III pressure plays an important rôle. (See Fig. 7, rate 4.)

Associated with every voltage is a pressure at which the system is in a steady state. (See Fig. 7, rate 4.) This corresponds perhaps to the conditions at which the rate of decomposition is being balanced by a rate of synthesis. This would be an explanation for the negative rates recorded in curve II of Fig. 6. If the system is in a steady state, decreasing the voltage of the bombarding electrons favors the synthesis of sodium azide and therefore a decrease in pressure. If sufficient time were allowed the system would reach a steady state at the new voltage. Whether this synthesis occurs at all potentials or only above some critical potential of nitrogen is not known. The lowest potential at which it was observed was 23 volts. The decomposition rates are so low at low voltages that it would be a matter of several hours before a steady state could be attained.

Attempts were made to study the synthesis of sodium azide by electron bombardment of a sodium and nitrogen mixture. It was impossible to attain equilibrium conditions due to the ability of metallic sodium to clean up nitrogen and to the great sensitivity of the clean-up to temperature. However, Moldenhauer and Möttig[26] have reported this synthesis at pressures of 15–25 mm under an electric discharge. If rate 12 of group III had been determined at lower pressures, the value of S/I_p would have been much greater. This rate was recorded at the highest pressure used for any of the determinations, namely 5×10^{-4} mm.

PHOTOCHEMICAL DECOMPOSITION

Experimental

An aqueous sodium azide solution was evaporated on one side of a quartz tube. The tube was sealed on the vacuum line and heated for 24 hours at a temperature of 200°C to remove water vapor. Had the temperature been much higher, some of the sodium azide would have decomposed thermally.

Data

The decomposition under the full mercury arc was quite rapid. It was also shown to occur when using a piece of glass $\frac{1}{8}$ inch thick, as a filter.

TABLE VII.

Distance of source	$1/D^2$	Rate of reaction	Aver. rate	Rate $\times D^2$
12.2 cm	0.00672	2 and 3.5	2.75	409
19.35 cm	.00267	0.96 and 1.03	0.995	373
22.65 cm	.00195	.65 and 0.71	.68	354
33.50 cm	.000891	.31 and .32	.315	353

[26] Moldenhauer and Möttig, Ber. **B62**, 1954–9 (1929).

By means of filters, the threshold wave-length for decomposition was found to be around 405 $m\mu$. No decomposition was observed for light of wave-lengths greater than this.

The rate of decomposition with the light from the full mercury arc, was directly proportional to the intensity. (See Table VII.)

The first two values of rate $\times D^2$ are higher. This is a breakdown of the inverse square law for a source of finite size.

Electronic Structures of Polyatomic Molecules and Valence. V. Molecules RX_n

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Theory. The approximate construction, for shared electrons in molecules RX_n, of molecular orbitals ("orbital" means one-electron orbital wave function) as linear combinations of atomic orbitals is discussed and illustrated by equations for RX_2, RX_3, RX_4 types. Properties of bonding, nonbonding, antibonding, also excited, molecular orbitals are described. *Valence* orbitals include both bonding and nonbonding types. RH_3 and H_3 orbitals are given as examples. Molecular orbitals constructed from atomic orbitals contain undetermined coefficients and implicit parameters (effective Z's of the atomic orbitals) which make them very flexible. They are useful for a qualitative theory which can be compared with empirical, especially chemical and spectroscopic, data. They also have value in semi-quantitative calculations (Van Vleck). **Applications.** Electronic structures, ionization potentials, form and stability (at least some of these properties in each case) of the molecules CH_4, NH_3, H_2O, NH_4, CH_3, NH_2, BeH_2, RX_n are described and interpreted in terms of molecular orbitals. It is shown that an electronic structure $1s^2 2[s]^2 2[p]^6$, closely related to that of the Ne atom, can be assigned to CH_4 without the least necessity or justification for departing from the idea of the equivalence of the four C−H bonding directions. This seems in some respects more natural than the Pauling-Slater method in which four equivalent bonds are obtainable only with mixtures of $2s$ and $2p$ carbon orbitals. The structures assigned for NH_3 and H_2O are also related to that of Ne, and that for NH_4 to that of Na. The ionization potential of NH_4 is estimated as 4.5 volts, slightly greater than for the K atom. The *proton affinity* of NH_3 (energy change for $NH_3 + H^+ \rightarrow NH_4^+$) is estimated to be 9 volts. The ionization potential of CH_3 is roughly estimated as 8.5 volts, and the energy of formation of CH_4 from $CH_3 + H$ is discussed. Whether molecules RX_3 are plane or pyramidal can be considered to depend on the quantitative outcome of a conflict of different factors; three such factors are noted. The first of these gives an explanation of Zachariasen's rule. Empirical evidence is cited showing that the geometrical possibilities of forms RX_4 tend to produce stabler electron configurations than are permitted by the possible geometry of RX_3. The ultraviolet absorption spectra of CH_4, NH_3, and H_2O are discussed in relation to the ionization potentials of these molecules.

A. INTRODUCTION

PAPERS I, II, III, and IV of this series were published in the *Physical Review*.[1] Paper I is a preliminary summary, correct except for a few details which are not vital, of the results to be given in II–VIII. Paper II, in which the viewpoint is strongly chemical, includes a brief critical review and comparison of theories of valence and the electronic structures of molecules. It is there pointed out that the present approach, although not stressing the idea of electron-pair bonds as does the theory of Pauling and Slater, is in some respects closer than the latter to the Lewis theory of valence, most of whose essential features are still valid as a summary and interpretation of the facts of valence. The present viewpoint and that of Slater and Pauling illuminate the Lewis theory from more or less complementary directions. Paper III and the last part of IV are devoted to the quantum theory of C_2H_4, which is taken as the prototype of the ordinary C=C double bond; and a theory of the mechanism of the photochemical *cis-trans* conversion is suggested. The first part of IV is devoted mainly to the quantum classification of electronic states of polyatomic molecules (analogous to the classifications S, P, D, $\cdots$ Σ, Π, Δ, $\cdots$ for atoms and diatomic molecules) with the aid of easily understood but powerful group theory methods. This classification is used as a basis for the descriptions of electronic structures in III, IV and the later papers.

B. THEORY

1. Introduction

A number of important molecules of the types RX_n, RX_mY_n, $RX_n \cdot RX_n$, $RX_lY_m \cdot RX_n$ and so

* This paper is based largely on work done during tenure of a John Simon Guggenheim Memorial Foundation Fellowship.

[1] R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751 (1932); **43**, 279 (1933).

on can be described by using, for the valence electrons, molecular orbitals which may be called molecular *valence orbitals*. These can be constructed in zeroth approximation as linear combinations of atomic orbitals of the atoms R, X, Y, ··· (method of Bloch and Hund). Only R atoms with s and (or) p valence electrons are considered in the present paper, and all atoms of any one kind X or Y near any R are assumed to be equidistant from this R and otherwise equivalent.

Only 1s atomic orbitals are used for the case that X or Y represent H atoms. For X or Y atoms with p valence electrons, e.g., halogen atoms, good molecular valence orbitals can rather obviously be obtained if in the construction of the latter an atomic orbital $p\sigma$ is used for each X or Y atom, leaving on the latter a closed shell $p\pi^4$ of unshared atomic orbitals (cf. I of this series[1] for further discussion and examples). The axis with reference to which the atomic orbitals $p\sigma$ and $p\pi$ are chosen is of course the C−X or C−Y axis. In VII of this series it will be shown that the use of the $p\sigma$ and the exclusion of the $p\pi$ atomic orbitals in constructing molecular valence orbitals, although not rigorously justified, is usually a good practical approximation, but that in some cases (in particular, plane molecules RX_3) the $p\pi$ atomic electrons may be quite appreciably drawn into the sphere of valence activities.

In the present paper, (V), only molecules of the type RX_n, especially RH_n, are treated. In VI the types R_2X_n and $RR'X_n$ will be considered, and in VII the types with more than one kind of substituent X, Y.

When molecular orbitals are used, as here, each must belong to some representation of the symmetry group known or assumed for the molecule (cf. IV of this series[1]). The molecular orbitals given by Eqs. (1)–(7) below all conform to this requirement, as can be verified by testing (cf. IV) what happens to each under the operations of the symmetry group of the molecule in question.

2. Construction of RX_n molecular orbitals approximately from atomic orbitals

In constructing RX_n valence orbitals, the atomic valence orbitals for the $n+1$ participating atoms are first listed. In general these are: an s orbital of R, a degenerate set of three p orbitals of R, and a degenerate set of n orbitals (1s for H atoms, $p\sigma$ for other X atoms) belonging one to each of the X atoms. Zeroth approximation molecular orbitals, $n+4$ in number, are now constructed from these $n+4$ atomic orbitals. Some, in general, are bonding, some approximately nonbonding, some antibonding; some are degenerate, some nondegenerate. As will be explained below, not all are valence orbitals.—The procedure of forming $n+4$ zeroth approximation molecular orbitals from $n+4$ atomic ones which are in part only *approximately* degenerate is an example of a general method discussed by Slater (cf. IV, p. 281 and reference 9, p. 1111[1]).

If the number of outer s and p (valence) electrons originally possessed by R was m, then $(m+n)/2$,—or $(m+n+1)/2$ if $m+n$ is odd,—of the molecular orbitals just mentioned are occupied, in the normal state of the molecule, by the $m+n$ valence electrons. The orbitals occupied will of course be those of lowest energy, and are what is here meant by molecular *valence orbitals*. These always include bonding orbitals, but also often some approximately nonbonding orbitals (cf. the case of NH_3, Section 14).

In molecules such as H_2O or HF, where the s orbital of R is obviously not appreciably concerned in the bonding, it can best be omitted from the above procedure, so that one starts with only $n+3$ atomic orbitals. The s orbital of R then appears in the molecule as an atomic and therefore nonbonding type. A similar result would still be obtained, however, if the s R orbital were at first included as one of the $n+4$, since it would turn out, when the linear combinations were formed, that one of them would contain this s orbital with a coefficient nearly unity. In such cases it is obviously sensible to leave out the s R orbital, but in intermediate or doubtful cases like NH_3, it should be included.

3. Excited molecular orbitals

In contrast to molecular valence orbitals, we may refer to *excited* molecular *orbitals*. These are orbitals which occur only in excited states of a molecule, and are important for its spectrum. Excited orbitals include, among others, the remaining $(n+4)-(m+n(+1))/2$ molecular or-

bitals which were constructed above from the $n+4$ valence atomic orbitals. These are for the most part antibonding, with respect to *all* the R−H bonds. The occurrence and relations of the bonding, antibonding, and nonbonding orbitals formed from the $n+4$ atomic orbitals can be understood from the examples given in Eqs. (2)–(7) and from the detailed discussion of NH_3 in Section 14.

In regard to excited orbitals in general, it should be pointed out that, as in the well-known diatomic cases of He_2 and H_2, the higher excited states, corresponding to large orbits in the Bohr theory, may be expected to form Rydberg series. Just as in the case of H_2 or He_2, the excited electron can then be classified as *ns*, *np*, *nd*, $\cdots$, with some additional subdivision of types in accordance with representations of the symmetry group of the molecule (cf. IV).

In the low excited states, where the excited electron is in a molecular orbital whose dimensions are not much greater than those of the rest of the molecule, the relations should be less simple, and much predissociation might be expected, and is found. These lower excited molecular orbitals include some for which certain antibonding forms, obtained above as a by-product in connection with the construction of valence orbitals, may be fairly good approximations.

4. X_n molecular orbitals

In constructing the $n+4$ (or $n+3$) molecular orbitals obtainable as linear combinations of atomic orbitals of the R and X valence electrons, the following procedure is convenient. First we choose axes x, y, z appropriate to the assumed symmetry of RX_n. We then note that zeroth approximation molecular orbitals which belong to representations of the assumed symmetry group can be built up only from atomic orbitals, or linear combinations of these, which are themselves representations of this group. The s atomic orbital of R always belongs to such a representation (in fact to the identical representation, usually called a_1), while the three-foldly degenerate p orbitals of R can always be so chosen as to belong to such representations. Usually the forms p_x, p_y, and p_z (i.e., $F(r)$ times $\sin\theta\cos\phi$, $\sin\theta\sin\phi$, and $\cos\theta$, respectively) are suitable. Each of these, when R is assumed perturbed by a force-field having the assumed symmetry of RX_n, may belong to a different nondegenerate representation, or sometimes p_x, p_y together (i.e., $p\pi$) belong to a degenerate and p_z (same as $p\sigma$) to a nondegenerate representation. In certain cases, e.g., symmetry T_d as in CX_4, the original degeneracy of the p atomic orbital is not split up at all (cf. IV, Table II[1]).

From the n equivalent H atom 1*s* or X atom $p\sigma$ orbitals (cf. Section 1), we can get representations of the RX_n symmetry group *only* by forming linear combinations, n in number. These can be obtained uniquely without great difficulty, often by inspection. The resulting forms are zeroth approximation molecular orbitals of a molecule X_n (neutral or ionized) with its n X atoms arranged in accordance with the prescribed symmetry. (As will be seen in VII, however, certain other molecular orbitals built up from $p\pi$ atomic orbitals may sometimes also be important, for molecules X_n other than H_n.)

5. Molecular orbitals of X_3 and RX_3, symmetry D_{3h}

The procedure can be made clearer by considering as an example the type RX_3. We assume that the three X atoms form an equilateral triangle. Two cases are important, (*a*) R atom at the center of the triangle: symmetry $D_{3h}(D_{3h}=C_{3v}$ times $\sigma_h)$; (*b*) R atom displaced from the center along a line perpendicular to the plane of the triangle: symmetry C_{3v}. In either case a z axis is chosen through the R atom perpendicular to the plane (cf. Fig. 1a). The x and y axes can conveniently be chosen as shown in Fig. 1a. The R atom gives orbitals s, $p\pi$, and $p\sigma$ belonging respectively to the representations a_1', e', and a_2'' of D_{3h}, or to a_1, e, and a_1 of C_{3v}, as can be verified by means of Tables II, IV of IV.

Denoting the $p\sigma$ (or 1*s* if X is H) orbitals of the three X atoms by α, β, γ respectively (cf. Fig. 1a), the following three orbitals are found to be correct linear combinations.[2] (In the case

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 177, 219 (1933). Eqs. (1), (5)–(7) of the present paper have been obtained independently by Van Vleck (cf. reference 10 in his first paper). Van Vleck, proceeding more mathematically than here, frequently obtains results the same as or similar to those given in the present series.

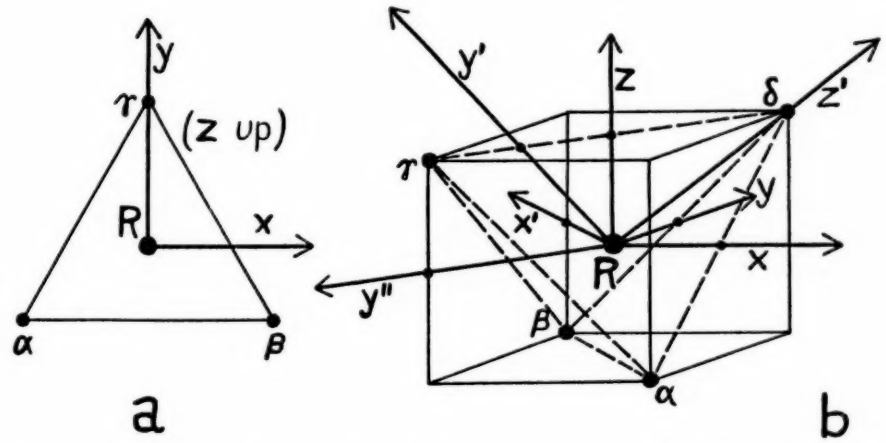

FIG. 1. (a) Arrangement of atoms and axes for RX_3 (cf. Eqs. (1)–(3)): α, β, γ are X atoms; the R atom is either in the center of the triangle (symmetry D_{3h}) or in front of it (C_{3v}) on the positive z axis, which extends toward the reader. (b) Arrangement of atoms and axes for RX_4 (symmetry T_d): α, β, γ, δ are X atoms at corners of a regular tetrahedron (edges shown by dotted lines), with R in the center. Three sets of axes are shown, namely x, y, z; x', y', z'; x', y'', z (cf. Eqs. (5)–(7)). To show these clearly, the tetrahedron is shown inscribed in a cube, and intersection of each axis with a cube edge or face is shown by a dot.

of $p\sigma$ orbitals, it is to be understood that the positive axis of each is directed toward the R atom.) The first belongs to representation a_1' of D_{3h} in case a, or a_1 of C_{3v} in case b, while the other two are equivalent and belong to the degenerate representation e' of D_{3h} or e of C_{3v}.

$$X_3 \text{ orbitals} \begin{cases} a_1': (3^{-\frac{1}{2}})(\alpha+\beta+\gamma) \\ e': (2^{-\frac{1}{2}})(\alpha-\beta) \text{ and} \\ \quad (6^{-\frac{1}{2}})(\alpha+\beta-2\gamma), \text{ or any pair of mutually orthogonal linear combinations of these.} \end{cases} \quad (1)$$

If we consider the three X atoms alone without R, we must use the symmetry D_{3h}, not C_{3v}; for this, the axes of X atom $p\sigma$ orbitals must all lie in the X_3 plane, directed toward the center. Eqs. (1) then give zeroth approximation orbitals of X_3 (neutral or ionized). The a_1' type gives bonding between all three atoms. In the normal state of H_3^+, if this has symmetry D_{3h}, the type a_1' would be occupied by two electrons giving a stable molecule. The type e' is an excited type not tending to bond all three atoms together.

Turning to RX_3, we must combine the above X_3 orbitals with the R orbitals s, $p\pi$, $p\sigma$. This is simplest for symmetry D_{3h}. Following the rule that R and X_3 orbitals can be combined only if they belong to the same representation of the desired symmetry group,—for otherwise the combination would not belong to any representation of the group,—one obtains the following RX_3 orbitals:

$$\left.\begin{aligned} &[s]a_1' = c(s)+d(\alpha+\beta+\gamma) \\ &[\pi]e': \begin{cases} [x]=c'(p_x)-(3^{\frac{1}{2}})d'(\alpha-\beta) \\ [y]=c'(p_y)-d'(\alpha+\beta-2\gamma) \end{cases} \\ &[z]a_2'' = p_z \\ &[s]^*a_1' = c(\alpha+\beta+\gamma)-d(s) \\ &[\pi]^*e': \begin{cases} [x]^*=d'(p_x)+(3^{\frac{1}{2}})c'(\alpha-\beta) \\ [y]^*=d'(p_y)+c'(\alpha+\beta-2\gamma) \end{cases}. \end{aligned}\right\} \quad (2)$$

With the degenerate types $[\pi]$ and $[\pi]^*$, it is to be understood that instead of the forms given, any pair of mutually orthogonal linear combinations of them could be substituted, for instance $(2^{-\frac{1}{2}})([x]+i[y])$, $(2^{-\frac{1}{2}})([x]-i[y])$, in the case of $[\pi]$.

6. Notation and conventions

In Eqs. (2), each molecular orbital is introduced by a descriptive symbol $[s]$, $[\pi]$, or $[z]$ which suggests an orbital of the atom R to which the molecular orbital in question is more or less closely related. Following this a systematic symbol, e.g., a_1' in $[s]a_1'$, e' in $[\pi]^*e'$, is (or may be) given showing to what representa-

tion of the molecule's symmetry group the orbital belongs.

The signs in Eqs. (2) are based on the following *conventions:* the coefficients c, d, c', d' are intrinsically positive; H atom 1s orbitals are always positive; the positive axis of each X atom $p\sigma$ orbital is directed toward the central atom R; each R atom s orbital is intrinsically positive in the *valence region*, i.e., the region beyond its last nodal surface where, for a valence orbital of the unexcited molecule, it overlaps X atom orbitals; for the R atom orbitals p_x, p_y, p_z, the valence regions surrounding the positive and negative x, y, or z axes are always intrinsically positive or negative, respectively. [One could, of course, choose *all* the signs just oppositely.]

7. Bonding, nonbonding and antibonding orbitals

With the conventions just given, it will be found that in $[s]$ and $[\pi]$ of Eqs. (2) the X atom orbitals α, β, γ always have the same sign as the R atom orbitals in the regions where they overlap the latter strongly. This results in a bonding effect for every such region of overlapping (cf. II, IV of this series), so that $[s]$ and $[\pi]$ are *bonding* orbitals. This refers to the interaction of R with the X's; there are also bonding and antibonding actions *between* X atoms, but these are of less importance, since the latter are considerably farther away from one another than from R.

The $[z]$ orbital here is seen to be of necessity nonbonding, because for reasons of symmetry there is no X_3 orbital with which it can combine. This conclusion, however, although correct for RH_3, more or less loses its validity if X is not H, since for RX_3 with symmetry D_{3h} it is not a good approximation to neglect the $p\pi$ atomic orbitals of X in constructing RX_3 orbitals: cf. Section 1.

There remain the $[s]^*$ and $[\pi]^*$ orbitals, which are completely *antibonding* as regards the interaction between R and the X atoms, since the R and X orbitals overlap with opposed signs. The coefficients in $[s]^*$ and $[\pi]^*$ have been so chosen that, in zeroth approximation for very large distances of separation of X_3 from R, $[s]^*$ and $[\pi]^*$ are respectively orthogonal to $[s]$ and $[\pi]$.

8. Some general considerations; undetermined coefficients and implicit parameters in the present method

The forms given in Eqs. (2) contain undetermined coefficients which make them capable of describing molecules with various degrees of strength of bonding between R and the X atoms, and various degrees of internal polarity or of approach to polar binding. Also, the atomic orbitals used implicitly contain undetermined parameters, e.g., Z_{eff}'s, since the atomic orbitals which would give the best approximate valence orbitals would not in general be orbitals appropriate to exactly neutral atoms, but rather to something intermediate between these and orbitals of (positive or negative) ions. In describing molecules of varying degrees of internal polarity, both the parameters and the coefficients would need to be varied. For ionized molecules the zeroth approximation valence orbitals, although formally the same as for corresponding neutral molecules, must in general have different coefficients and implicit parameters.

For the relatively simple case of H_2, this problem has been discussed by Hund.[3] In H_2 the two valence electrons occupy a valence orbital which may be described as $\alpha+\beta$. One gets a much more nearly correct description of the electronic structure if one takes for α and β not ordinary 1s orbitals of neutral H ($Z_{eff}=1$), but 1s orbitals intermediate between those of H and H^- ($Z_{eff}<1$). Similar but more complicated effects must appear in molecules RX_n.

Because of the undetermined coefficients and implicit parameters, and because of the approximation still involved in constructing molecular orbitals from even the best possible atomic orbitals, forms such as those given in Eqs. (1)–(7) are, as they stand, only of qualitative significance. This, however, does not deprive them of power to give insight into electronic structures of molecules and a good idea of some of the energy states to be expected when the molecules are excited or ionized. Thus they furnish a qualitative theoretical framework with which empirical results can be compared and into which they can be fitted, analogous to that which has been successfully used for the quali-

[3] F. Hund, Zeits. f. Physik **73**, 1 (1931).

tative theory of diatomic molecules and their spectra.

One can also hope in individual cases, using simplifying assumptions, to make useful more or less quantitative calculations starting with molecular orbitals. This procedure is, to be sure, not well adapted to calculations of absolute energy or energies of dissociation,[3] but, as especially Van Vleck has shown,[2] can give good results in determining the relative energies of a molecule in different geometrical forms, so that the most stable form, and the valence angles, can be predicted.

9. Molecular orbitals of RX_3, symmetry C_{3v}

After this brief general discussion, we return to the problem of the RX_3 orbitals, now assuming the symmetry C_{3v}. The forms for the special case RH_3 are now as follows:

$$\left.\begin{aligned} &[s]a_1 = c(s) + d(\alpha+\beta+\gamma) - g(p_z) \\ &[\pi]e\text{: as } [\pi] \text{ in Eqs. (2)} \\ &[z]a_1 = c''(p_z) - d''(\alpha+\beta+\gamma) + g''(s) \\ &[\pi]^*e\text{: as } [\pi]^* \text{ in Eqs. (2)} \\ &[s]^*a_1 = c^*(\alpha+\beta+\gamma) - d^*(s) + g^*(p_z) \end{aligned}\right\}. \quad (3)$$

In Eqs. (3), contrary to the usual conventions (Section 6), the coefficients d'', g'', g^*, d^* are not necessarily always positive quantities. Their signs and magnitudes depend on how far the R nucleus is from the H_3 plane, and on the nature of the atom R. If R is near the H_3 plane, d'' and all the g's are nearly zero (cf. Eqs. (2)).

In the case of X atoms with p valence electrons, Eqs. (3) are not always very good approximations, except for $[\pi]$ and $[\pi]^*$. Modifications along the lines suggested in Section 7 for $[z]$, and in Section 1, may be needed.

10. Molecular orbitals of RX_2, RX_4

By methods similar to those used for RX_3, the valence orbitals for RX_2 and RX_4 given by Eqs. (4)–(7) are obtained. Other, excited, orbitals obtainable from the same atomic orbitals (cf. Sections 2, 3 above) can also be written down very easily. In the RX_4 case, for instance, where all the valence orbitals are bonding (cf. Section 6), an equal number of antibonding orbitals exists, namely one $[s]^*$ and one $[p]^*$. The orbital $[s]^*$ is obtained from $[s]$ of Eqs. (5) by substituting d, $-c$ for c, d, while $[p]^*$ is obtained from $[p]$ by putting d', $-c'$ for c', d'; these coefficients, however, are applicable only for large distances of the 4 X from the R. Actually it seems likely that atomic orbitals $3s$ and $3p$ (cf. Section 11) would be better approximations to excited orbitals of CH_4 than $[s]^*$ and $[p]^*$ would be.

In each case in Eqs. (4)–(7) the origin is taken at the R nucleus. In the RX_4 case, the positions of the axes relative to the X nuclei α, β, γ, δ are as shown in Fig. 1b.

Degenerate molecular orbitals can of course be written in an infinite variety of ways. It is of interest here to write down various forms which constitute correct zeroth approximations for distortions of the original symmetry. This is done below for the $[p]$ valence orbitals of RX_4. They are first given, in Eqs. (5), in forms which are natural for symmetry T_d. In Eqs. (6) and (7) they are given in forms which, while still appropriate to T_d, are suitable zeroth approximations when the molecule is perturbed or its symmetry is distorted, e.g., by displacing one, or two, X atoms from their positions of equivalence with the others, in such a way as to give the lower symmetry C_{3v} or C_{2v}. As will be seen in VI and VII of this series, Eqs. (6), (7) form starting points for the consideration of derivatives RH_3X, RH_2X_2, RX_2Y_2, etc., and for an understanding of relations between RH_3X and RH_3, and so on (cf. also Van Vleck's recent papers[2]).

Type RX_2, symmetry C_{2v} (triangular form): see IV of this series, Eqs. (8).

Type RX_2, $D_{\infty h}$ (linear form; α on the positive, β on the negative, y axis):

$$\left.\begin{aligned} &[s]\sigma_g = c(s) + d(\alpha+\beta); \\ &[y]\sigma_u = c'(p_y) + d'(\alpha-\beta) \end{aligned}\right\}. \quad (4)$$

Type RX_4, T_d (regular tetrahedron); cf. Fig. 1b for axes x, y, z:

$$\left.\begin{aligned} &[s]a_1 = c(s) + d(\alpha+\beta+\gamma+\delta) \\ &[p]t_2: \begin{cases} [x] = c'(p_x) + d'(\alpha-\beta-\gamma+\delta) \\ [y] = c'(p_y) + d'(-\alpha+\beta-\gamma+\delta) \\ [z] = c'(p_z) + d'(-\alpha-\beta+\gamma+\delta) \end{cases} \end{aligned}\right\}. \quad (5)$$

Type RX_4, T_d, zeroth approximations for C_{3v}; cf. Fig. 1b for new axes (x', y', z'):

$$[p]'t_2:\begin{cases}[x]'=(-2^{-\frac{1}{2}})([x]-[y]) \\ \quad =c'(p_{x'})-2^{\frac{1}{2}}d'(\alpha-\beta) \\ [y]'=(-6^{-\frac{1}{2}})([x]+[y]-2[z]) \\ \quad =c'(p_{y'})-(2/3)^{\frac{1}{2}}d'(\alpha+\beta-2\gamma) \\ [z]'=(3^{-\frac{1}{2}})([x]+[y]+[z]) \\ \quad =c'(p_{z'})-(3^{-\frac{1}{2}})d'(\alpha+\beta+\gamma-3\delta)\end{cases}. \quad (6)$$

Type RX_4, T_d, zeroth approximations for C_{2v}; cf. Fig. 1b for axes (x', y'', z):

$$[p]''t_2:\begin{cases}[x]' \text{ as in (6)} \\ [y]''=(-2^{-\frac{1}{2}})([x]+[y]) \\ \quad =c'(p_{y''})+(2^{\frac{1}{2}})d'(\gamma-\delta) \\ [z] \text{ as in (5)}\end{cases}. \quad (7)$$

11. Approximation of RH_n orbitals by central-field orbitals. Comparison with electron-pair bonds

In tetrahedral molecules RX_4, in particular CH_4, the advantages of describing the state of the valence electrons by means of molecular orbitals are particularly obvious.[3a] Since the symmetry of a tetrahedron approaches that of a sphere, $2s$ and $2p$ orbitals of an atom with suitably chosen nuclear charge should be rather good approximations to CH_4 molecular orbitals; probably orbitals of the O atom would do very well. (For the $1s$ electrons, C atom orbitals would of course be used.) Better still would be orbitals corresponding to the field set up by a C nucleus surrounded at a distance of about 1.1×10^{-8} cm by a thin uniform shell of positive electricity of total charge $4e$, allowance being of course made also, by the Hartree method, for the average effect on any one electron of the remaining electrons. With either of these models, the electron configuration and state of unexcited CH_4 would be described as $1s^2\,2s^2\,2p^6$, ^1S.

To investigate the effect of the tetrahedral symmetry of CH_4, a perturbation of the second model can be introduced which gradually concentrates the positive shell into four H nuclei. The group theory treatment shows that this does not alter the three-fold degeneracy of the $2p$ orbitals nor allow these to hybridize with $2s$. For according to Table II of IV (cf. note b of the table), $2s$ and $2p$ go over for tetrahedral symmetry (T_d) into examples of types a_1 and t_2, respectively (cf. Table I of IV for the properties of these). Since these CH_4 orbitals are closely related to the unperturbed central-field orbitals $2s$ and $2p$, they may appropriately be called $[s]a_1$ and $[p]t_2$.—The excited orbitals of CH_4, especially if CH_4^+ still has the symmetry of a regular tetrahedron (cf. end of Table I), should be very nearly like atomic orbitals $3s$, $3p$, $\cdots$.

A similar approach can be made for the molecules NH_4^+, NH_3, H_2O, and so on, starting with s and p orbitals and applying a perturbation having the final symmetry. Except where the latter is tetrahedral, it causes the p type to split up into either two or three types, one of which in most cases can hybridize more or less with s. What happens in each case can be determined by the group theory method.

From the above approach, it appears that the relative advantages of the method of molecular orbitals are greatest as compared with the method of electron-pair bonds for molecules whose symmetry is high and so approaches that of an atom (SF_6, CH_4, MnO_4^-, and to a less extent NH_3, NO_3^-, and the plane molecule $PtCl_4^=$), and are *least* with *diatomic* or linear molecules. Since molecular orbitals have been successfully used for diatomic molecules, they should then be all the more appropriate for more symmetrical molecules. One sees also that the use of molecular orbitals is relatively simple and natural in cases where more than one type of valence electron of a central atom is in use (e.g., s and p in CH_4, s and dt_2 in MnO_4^-), and where Pauling and Slater, in forming electron-pair bonds, have used hybrid atomic orbitals (cf. Van Vleck[2] for a critical discussion).

C. RH_n Molecular Orbitals. Applications

12. Electronic structures and ionization potentials of molecules RH_n

In Table I the normal state of each of several molecules RH_n is described in terms of the

[3a] Cf. also G. Glockler, J. Am. Chem. Soc. **48**, 2021 (1926), and H. Grimm, Zeits. f. Elektrochemie **31**, 474 (1925) for a viewpoint resembling the present one.

valence orbitals given in Sections 5, 9, 10. In each case there are of course also the two K electrons $1s^2$. The type $1s$ may be regarded either as an atomic orbital or as a molecular orbital belonging to the identical representation (a_1 or a_1').

The experimentally known symmetry[4, 5] is assumed in the cases of H_2O and CH_4, while two possible alternative symmetries are given in those of BeH_2 and BH_3. The molecule NH_3 is known to have a low-pyramidal form (height of pyramid about 0.38×10^{-8} cm, energy required to make it plane about 0.25 volt).[6] Hence although the symmetry is really C_{3v}, NH_3 is so nearly plane that the corresponding symmetry D_{3h} is perhaps more important. Both cases are covered in Table I.

The normal and the predicted lowest one or two states of some ions RH_n^+ are also described in Table I, and observed ionization potentials of RH_n molecules are matched against these predicted RH_n^+ states (cf. preliminary account in I of this series). Where observed potentials are lacking, estimated values are given.

In connection with the experimental ionization potentials (the estimated values are intended to be on the same basis), it should be noticed that each of these probably corresponds approximately, in accordance with the extended Franck-Condon principle, to a process in which an electron is removed without change in the dimensions of the molecule. The adiabatic or strict minimum ionization potentials may be considerably lower in some cases. For understanding the structures of the neutral molecules RH_n, however, their non-adiabatic observed potentials are really more useful than adiabatic ones would be.

A comparison of the ionization potentials of CH_4, NH_3, H_2O with those of the atoms C, N, O is instructive. (HF and F would also be of interest, but data are lacking.) In order to have comparable results the change in multiplicity during ionization should be the same in all cases, as also, so far as possible, the multiplicities themselves. In the case of all the three molecules, one starts with a singlet state $^1A_1$ and gets a doublet ionic state. The observed potentials are 14.4, 11.1 and 13 volts, respectively. For the atoms the best comparable figures are: C(weighted average of ^1D and ^1S of s^2p^2)$\rightarrow$ $C^+(s^2p, {}^2P)$, 9.8 volts; N(w. ave. ^2D, ^2P of s^2p^3) $\rightarrow N^+({}^3P$ of $s^2p^2)$, 11.7 volts; O(w. ave. ^1D, ^1S of $s^2p^4)\rightarrow O^+$(w. ave. ^2D, ^2P of s^2p^3), 15.2 volts.

The relatively high value for CH_4 is evidently a consequence of the fact that the $[p]$ type is not split up. (The possibility,—cf. end of Table I,—that CH_4^+ has a different symmetry than CH_4 is not important for the observed ionization potential if it is non-adiabatic.) It will be noted that, judging from the ionization potential, the $[p]$ electrons in CH_4 are bound nearly as firmly as p electrons in the O atom. The low values for the other molecules RH_n, lower even than for the atoms R, are evidently consequences of the splitting up of the $[p]$ type into $[\sigma]$ and $[\pi]$ in NH_3, or $[z]$, $[y]$, and $[x]$ in H_2O, of which the observed minimum potential corresponds to the most loosely bound type. The latter is clearly $[\sigma]$ in NH_3, $[x]$ in H_2O.

In the case of NH_3 the argument is as follows. Assuming for simplicity that NH_3 is plane, as is nearly true, we see that only the $[s]$ and $[\pi]$ orbitals have hydrogen-bonding power, the $[z]$ orbitals being, in zeroth approximation, pure N atom orbitals (cf. Eqs. (2)). The bonding orbitals $[s]$ and $[\pi]$ are all concentrated near the plane of the four nuclei, especially in the regions between the N nucleus and the H nuclei. Brief consideration indicates that while the $[s]$ and $[\pi]$ orbitals are mainly in regions of lower potential than for a free N atom, the $[\sigma]$ orbitals are mainly in a region of relatively higher potential near the z axis, and should be less firmly bound. A similar argument applies to the $[x]$ orbitals in H_2O. These are in zeroth approximation pure O atom orbitals (cf. Eqs. (8) of IV).—It should be noted that the actual departure of normal NH_3 from planeness is enough to make the observed ionization potential, although it is strikingly low, considerably higher than would otherwise probably have been expected (cf. Table I, and note**).

NH_4 (known as an unstable substance in

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[4] Cf. R. Mecke, Zeits. f. Physik **81**, 313, 445, 465 (1933) for recent exact results.

[5] Cf. E. Teller and L. Tisza, Zeits. f. Physik **73**, 791 (1932) for removal of last difficulties.

[6] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932); N. Rosen and P. M. Morse, Phys. Rev. **42**, 210 (1932); E. Fermi, Rend. Lincei **16**, 179 (1932).

TABLE I. *Electronic states and ionizing potentials (all normal states, unless otherwise indicated).*

H_2O (symm. C_{2v}, isos. triangle):	$([s]a_1)^2([y]b_2)^2([z]a_1)^2([x]b_1)^2$,	$^1A_1$
H_2O^+ (13.2 volts*):	$(\ )^2(\ )^2(\ )^2(\ )$,	$^2B_1$
H_2O^+ (16 volts?†):	$(\ )^2(\ )^2(\ )(\ )^2$,	$^2A_1$
	$(\ )^2(\ )(\ )^2(\ )^2$,	$^2B_2$
NH_2 like H_2O^+; CH_2, configuration like H_2O minus $([x]b_1)^2$, normal state $^1A_1$.		
BeH_2 (linear, according to Zachariasen's rule[7]): $([s]\sigma_g)^2([y]\sigma_u)^2$,		$^1\Sigma^+_g$.
NH_3 (symm. C_{3v}, triang. pyramid):	$([s]a_1)^2([\pi]e)^4([z]a_1)^2$,	$^1A_1$
NH_3^+ (11.1 volts*):	$(\ )^2(\ )^4(\ )$,	$^2A_1$
NH_3^+ (17 v estimated):	$(\ )^2(\ )^3(\ )^2$,	^2E
$NH_3(D_{3h}$, plane):	$([s]a_1')^2([\pi]e')^4([z]a_2'')^2$,	$^1A_1'$
NH_3^+ (10.4 v est.**):	$(\ )^2(\ )^4(\ )$,	$^2A_2''$
NH_3^+ (18 v est.**):	$(\ )^2(\ )^3(\ )^2$,	$^2E'$
H_3O^+ like NH_3; CH_3 like lowest NH_3^+, $^2A_1$ or $^2A_2''$; CH_3^+ and BH_3, configuration like NH_3 minus $([z]a_1)^2$ or $([z]a_2'')^2$, state $^1A_1$ or $^1A_1'$; according to Zachariasen's rule,[7] BH_3 should be plane.		
CH_4 or NH_4^+ (symm. T_d, tetrahedron):	$([s]a_1)^2([p]t_2)^6$,	$^1A_1$
CH_4^+ (14.4 volts):	$(\ )^2(\ )^5$,	$^2T_2$

[According to Van Vleck[2] it is probable that CH_4^+ in equilibrium has the symmetry V_d. In this case the $[p]t_2$ type would break up (cf. Table IV of IV) into two types $[\pi]e$ and $[z]b_2$, giving two adiabatic ionization potentials of CH_4, corresponding to two states $\cdots e^3b_2^2$, ^2E and $\cdots e^4b_2$, $^2B_2$ of CH_4^+. The second of these should be considerably lower than the single observed potential, which as already noted presumably corresponds to nonadiabatic ionization with symmetry T_d.]

* Cf. Landolt-Börnstein, *Physisch-Chemische Tabellen*, 5th Edition, Ergänzungsband 2, p. 575 (Berlin, Springer, 1931) for the observed ionization potentials.

† Cf. H. D. Smyth and D. W. Mueller, Phys. Rev. **43**, 116 (1933). Estimated values, however, about 19, 20 volts.

** These estimated values are based on the reasonable assumption (cf. section 14) that the actual equilibrium form of NH_3^+ is plane.

solution in mercury: cf. textbooks of inorganic chemistry) should have its last electron in a molecular orbital closely resembling a 3*s* atomic orbital of O or F, probably most nearly like the latter. Corresponding to this, the ionization potential of NH_4 may be estimated as 4.5 volts. NH_4 is to CH_4 as Na to Ne. Chemically NH_4 most resembles potassium, a fact in agreement with the estimated ionization potential, which is slightly greater than that of potassium.

The temporary existence but rapid decomposition of NH_4 dissolved in Hg suggests that an isolated NH_4 molecule may be physically stable, but that the reaction $2NH_4 \rightarrow 2NH_3 + H_2$ is responsible for the decomposition. (Quite possibly, however, even an isolated NH_4 molecule might predissociate, i.e., soon decompose spontaneously, into $NH_3 + H$.) If one assumes the energy change for $NH_3 + H \rightarrow NH_4$ to be about zero, then from the known or estimated ionization potentials of H and NH_4, one finds the extremely high energy change 9.0 volts for $NH_3 + H^+ \rightarrow NH_4^+$.

Strong support for this value is obtained if one calculates it by a cyclic process. Making use of an estimated lattice energy for NH_4Cl of 163 kcal. = 7.06 volts (same as for RbCl, whose lattice has about the same dimensions and similar interionic forces), assuming an electron affinity of 86 kcal. = 3.72 volts for Cl as derived from lattice energy estimations, and using other necessary data (all accurately known), one gets 8.96 volts for $NH_3 + H^+ \rightarrow NH_4^+$ (proton affinity of NH_3). This would correspond to zero energy change for the decomposition $NH_4 \rightarrow NH_3 + H$, in agreement with the assumption made above.

According to Hogness and Kvalnes (reference 4 of I), when CH_4 is bombarded with electrons CH_4^+ appears at about 14.5 volts, then CH_3^+ at about 15.5 volts. At 15.5 volts the CH_4^+ ions must, then, have at least enough excitation energy to allow the predissociation process $CH_4^+ \rightarrow CH_3^+ + H$. If this is nearly adiabatic, as seems possible, then if we can estimate the adiabatic ionization potential of CH_3, we can calculate the (adiabatic) energy change ΔE for the dissociation $CH_4 \rightarrow CH_3 + H$, since the adiabatic ΔE's for the two processes $CH_4 \rightarrow CH_3 + H \rightarrow CH_3^+ + H$ and $CH_4(\rightarrow CH_4^+) \rightarrow CH_3^+ + H$ must be the same. The adiabatic ionization potential of CH_3 may be estimated (cf. the potentials given above for C and N) as 2 volts less than the value NH_3 would have if it had the same shape as CH_3. Most probably CH_3 has a low-pyramidal or perhaps a plane shape, and CH_3^+ a plane form (cf. Van Vleck[2] and Section 14). For plane CH_3, the estimated (adiabatic or non-adiabatic) potential is 8.4 volts. For a low-pyramid form like that of NH_3, if CH_3^+ is plane, about 8.7 volts is obtained. From such values as these, we find for the ΔE of $CH_4 \rightarrow CH_3 + H$ about 7 volts, which is remarkably

[7] W. H. Zachariasen, Phys. Rev. **37**, 775 (1931); J. Am. Chem. Soc. **53**, 2123 (1931).

large compared with the *average* value of about 4 volts per H atom for the formation of CH_4 from C+4H.

If, however, the CH_3^++H formed from CH_4 at 15.5 volts possess kinetic and the CH_3^+ internal energy, the above value is correspondingly lowered. If for instance the newly formed CH_3^+ had in the first moment the same shape as if it were still part of CH_4, it would thereby possess vibrational energy of probably 1 or 2 volts as compared with CH_3^+ in equilibrium. Since it seems improbable that the products CH_3^++H produced at 15.5 volts carry away more than 2 volts energy as a result of departure from adiabatic conditions, we find that $CH_4 \rightarrow CH_3+H$ probably takes at least 5 volts.

In I it was pointed out that the energies of formation *per hydrogen atom*, in kilocalories, are about 148, 110, 87, 91 for HF, H_2O, NH_3, CH_4, and that the value for CH_4 is conspicuously higher than one would get by an extrapolation from the other three values.[8] To the above series can now be added the figures (79) and 123 kcal. per H atom for $C+3H \rightarrow CH_3$ and $N^+ + 4H \rightarrow NH_4^+$, which can be calculated assuming 5 volts for $CH_4 \rightarrow CH_3+H$ and using 9 volts for $NH_3+H^+ \rightarrow NH_4^+$. From these results and from the general chemical evidence on the high stability of molecules and ions RX_4 compared with RX_3, one sees the importance of the *number* of centers X (the coordination number) for the stability of electron structures. Apparently, other things being equal, the arrangement of four X around an R allows the valence electrons to settle down considerably more firmly than does that of three X in either a plane or a pyramidal RX_3. The theoretical reasons for this are not obvious. Perhaps they depend on a lessening of the average electronic repulsions in RX_4 because of the high symmetry which is possible.

The high values found in preceding paragraphs for the energies of the reactions $NH_3+H^+ \rightarrow NH_4^+$ and $CH_3+H \rightarrow CH_4$ have been seen to agree with the above conclusions. The strong tendency of NH_3 to form NH_4^+ and other complexes can also be understood from another point of view: it can be attributed directly (cf. I and II) to the resulting stabilization of the two loosely bound nonbonding [*z*] electrons of NH_3, which usually enter into one-sided ("semi-polar") bonds. Presumably there is a connection between the relatively low energy of formation of NH_3 from N+3H and the existence in it of the loosely-bound [*z*] electrons. It is, however, probably incorrect to attribute the former, as was done in I, simply to the fact that it contains these [*z*] electrons.

It might be suggested that it is the greater availability of the *s* electrons for valence purposes in CH_4 than in NH_3 (cf. Section 14), rather than the geometrical possibilities, which makes CH_4 relatively so stable. The high energies of formation of NH_4^+ from NH_3 and of CH_4 from CH_3, also the instability of BH_3 (where the availability of the *s* electrons is even greater) as against B_2H_6, all give evidence against this.

13. RH_n absorption spectra

The observed ionization potentials of H_2O, NH_3, CH_4 are 14.4, 11.1, 13 volts. If the lowest excited state of each of these molecules is obtainable by adding an electron in the same type of excited molecular orbital (presumably 3*s*) to the molecule ion, then one might expect the frequencies at which the corresponding ultraviolet absorption spectra begin, to run roughly parallel to the ionization potentials. The energy of binding of a 3*s* orbital should probably increase slightly from CH_4 to H_2O, with an average value of about 4.5 volts (cf. NH_4 in Section 12). Such a 3*s* orbital should be large enough to be atom-like, resembling a penetrating 3*s* orbital of excited O, F, or Ne.

Actually it is true that NH_3, with the lowest ionization potential, does show marked absorption at considerably longer wave-lengths than H_2O or CH_4. The NH_3 absorption consists of a long series of bands of which those at longest wave-lengths (λ2360 to λ2213) show evidence of fine structure, while toward shorter wave-lengths the bands become diffuse, corresponding to fairly strong predissociation, at the same time in-

[8] The values for NH_3 and CH_4 may be in error by as much as 2 or 3 kcal. because of uncertainty as to the heat of dissociation of N_2 (here the value 194 kcal. was used) and as to the heat of sublimation of carbon (141 kcal. used here) and its interpretation. These uncertainties do not affect the qualitative conclusions reached here. The values here are revised as compared with R. Mecke, Zeits. f. physik. Chemie **7**, 108 (1930).

creasing rapidly in intensity to a very strong plateau or maximum at and below λ2000.[9, 10] The bands are accompanied by a continuous background. If the excited state involved is thought of as obtained by adding an excited electron to NH_3^+ (11.1 volts), then the energy of binding of this electron is about 5 volts, approximately what we expected for a 3*s* orbital. This value is obtained by taking an energy of excitation of 6.2 volts, corresponding to about λ2000, where the absorption is strong (beginning of Franck-Condon maximum). This is the proper thing to do, since the observed ionization potential 11.1 volts probably corresponds to the beginning of fairly strong ionization (Section 12).

At one atmosphere pressure with a 15 mm path, CH_4 shows complete absorption from λ1800 down.[10] (Under the same conditions NH_3 shows complete absorption below about λ2150.[10]) This continuous spectrum presumably represents a dissociation or predissociation process. The same explanation may reasonably be suggested for the strong continuous band which, beginning suddenly near λ1800, initiates the ultraviolet absorption of H_2O vapor.[10] Apparently it happens only in NH_3 that the ionization potential is low enough to permit the spectrum to begin with transitions to an excited state which is in some degree stable. The unstable states which give rise to continuous absorption can perhaps best be thought of as repulsion states of $RH_{n-1}+H$ or $RH_{n-2}+H_2$.

14. Electronic structure and form of RX_3 molecules

According to Zachariasen's rule[7] as applied to RX_3 molecules, these are plane (D_{3h}) if the number of valence electrons is just enough so that the molecule could be thought of as built up from rare-gas-form ions (examples $B^{+3}H^-_3$ and $N^{+5}O^{=}_3$), but pyramidal (C_{3v}) if more valence electrons are present (examples $C^{+3}H^-_3$, $N^{+3}H^-_3$, $Cl^{+5}O^{=}_3$, with one valence electron remaining on C^{+3}, two on N^{+3}, Cl^{+5}). The rule is confirmed in all observed cases,[7] including NO_3^-, NH_3, ClO_3^- but not yet BH_3 or CH_3.

It is now of interest to see whether the present formulation in terms of molecular orbitals would lead one to expect such results and if so, why. Comparing the electron configurations $1s^2[s]^2[\pi]^4$ of BH_3, $\cdots [\pi]^4[z]$ of CH_3, and $\cdots [\pi]^4[z]^2$ of NH_3 (cf. Table I), we see that if Zachariasen's rule is applicable here, it is the $[z]$ electrons whose presence or absence determines whether RH_3 is plane or pyramidal. Similarly NO_3^- (plane) and ClO_3^- (pyramidal) differ in that the former has no $[z]$ electrons, the latter two (cf. I, VII). A good reason why $[z]$ electrons tend to make RX_3 molecules pyramidal is to be seen in the fact that they are nonbonding for the plane form (Eqs. (2)) but can be strongly bonding (d'' large in Eqs. (3)) for high-pyramid forms.

For the types $[s]$ and $[\pi]$ the possibility of strong bonding is not so obviously dependent on whether the molecule is plane or pyramidal. It appears likely, however, that strong withdrawal of the R atom from the X_3 plane might reduce the bonding power of $[\pi]$, since the R atom p_x and p_y orbitals would then overlap the H orbitals α, β, γ less. From this discussion, it would seem to be a quantitative rather than a qualitative matter whether the presence of one or even two $[z]$ electrons suffices to make a molecule pyramidal. NH_3 is, of course, known to be pyramidal, but the pyramid is rather low (about 0.38A high[6]), so that it would seem quite possible that NH_3^+ and CH_3 as well as BH_3 might be plane.

The idea that the decision between a plane and a pyramidal form depends entirely on an equilibrium between opposing tendencies of $[z]$ and of $[s]$ and $[\pi]$ electrons needs qualification in two respects. (1) If one writes out the complete ψ of a molecule (cf. IV), using molecular orbitals for the shared electrons, then rearranges suitably, ψ can be expressed as a linear combination of a number of ψ's corresponding to a variety of ionic and electron-pair bond states. The former include states with R positive and one or more H's negative and others with R negative and one or more H's positive (cf. Van Vleck[2] for CH_4 as an example). For an essentially nonpolar molecule,

[9] Ferrières, Comptes Rendus **178**, 202 (1924); G. Landsberg and A. Predwoditeleff, Zeits. f. Physik **31**, 544 (1925); K. F. Bonhoeffer and L. Farkas, Zeits. f. physik. Chemie **134**, 337 (1929); V. Henri, Leipziger Vorträge 1931, p. 131 (S. Hirzel, Leipzig); J. K. Dixon, Phys. Rev. **43**, 711 (1933).

[10] S. W. Leifson, Astrophys. J. **63**, 73 (1926). For a correction in regard to CH_4, cf. R. Gräfin zu Dohna, Zeits. f. Physik **81**, 745 (1933).

there is a sort of even balance between the states with R positive and those with R negative (cf. H_2 in II, Section 13), but in general one of these sets preponderates more or less and the molecule can be called polar. In such cases, the molecule's shape evidently depends partly on polar forces. (2) So far we have neglected possible hybridization of $[s]$ and $[z]$, which for C_{3v} both belong to representation a_1. Such hybridization cannot occur for D_{3h} and is obviously unimportant for nearly plane forms and for atoms like O, F, Cl, but should be important for high-pyramid molecules with atoms like B, C, and perhaps also N. In the limiting case of complete mixing, which might occur if the $ns-np$ energy interval were negligible compared with energy effects associated with formation of molecular from atomic valence orbitals, we should have $g=c$, $g^*=d^*$, $c''=g''$ in Eqs. (3), so that $[s]$ would be $a(s-p_z)+b(\alpha+\beta+\gamma)$. By graphically adding s and $-p_z$ and renormalizing, one sees that $s-p_z$ in a pyramidal molecule gives much stronger overlapping with $(\alpha+\beta+\gamma)$ than does s in a plane molecule (g, $g^*=0$). Hence the bonding effects of $[s]$ for a high-pyramid molecule would be much stronger than for a plane molecule. At the same time $[z]$, which (since here $c''=g''$ in Eqs. (3)) would be of the form $a'(s+p_z)+$(or $-)b'(\alpha+\beta+\gamma)$, would be nearly nonbonding because $s+p_z$ overlaps $(\alpha+\beta+\gamma)$ very little. [When $g=c$, $\cdots$ as in the case considered here, the designations $[s]$, $[s]^*$, $[z]$ are really inappropriate, but in general, with $c>g$, $c''>g''$, $\cdots$ they are not unreasonable.]

In BH_3, it seems likely that the valence orbital $[s]$ could be of the strongly hybridized type (g nearly as large as c), so that quite possibly the molecule,—electron configuration $1s^2[s]^2[\pi]^4$,—is after all pyramidal contrary to Zachariasen's rule. In CH_3, with configuration $1s^2[s]^2[\pi]^4[z]$, the pyramidal form also seems likely, in agreement with Zachariasen's rule. It seems likely, however, that NH_3^+ is plane (cf. third paragraph of this section), since $s-p$ hybridization is probably negligible. If CH_3 is pyramidal, the type $[s]$ probably contains considerably more s than p_z and the type $[z]$ considerably more p_z than s. The type $[z]$ is very likely nearly nonbonding here, since it is always nonbonding for a plane RH_3 molecule and should be nearly so for the other limiting case of a pyramidal molecule with strong $s-p$ hybridization.

From the approximately known dimensions of the NH_3 molecule[6] one can draw some conclusions about its structure. In view of the relatively high Z and low-pyramidal form, we may probably neglect hybridization of $[s]$ with $[z]$, i.e., put $g\sim 0$ and $g''\sim 0$ in Eqs. (3). Because of the relatively high Z, it is probable that $[s]$ gives only a little H-bonding (c/d large compared with $3^{\frac{1}{2}}$ in Eqs. (3)). Because the pyramid is rather low, $[z]$ cannot give very strong H-bonding (c''/d'' fairly large compared with $3^{\frac{1}{2}}$ in Eqs. (3)). This leaves the $[\pi]$ electrons as the chief bonding electrons. Defining a nonpolar bond as consisting of two strongly bonding electrons, one may estimate that the NH_3 molecule has about $2\frac{1}{2}$ such bonds (two $[\pi]$ bonds, and one-half bond divided between $[s]$ and $[z]$).

The $[\pi]$ electrons would have maximum bonding power for $c'=6^{\frac{1}{2}}d'$ in Eqs. (3); this would correspond to equal participation of N and H orbitals in $[\pi]$. Assuming this relation,—of course it can hardly be exactly true,—and assuming d/c and d''/c'' quite small, the molecular configuration $[s]^2[\pi]^4[z]^2$ would correspond in its make-up to a preponderance of N atom over H atom orbitals, i.e., NH_3 would be somewhat polar with the N negative. It may then be that the deficiency in nonpolar bonds ($2\frac{1}{2}$ instead of the three assigned by ordinary valence theory and by the Pauling-Slater model with 90° valence angles) is made up by polar forces.

The Raman Spectrum of Water Vapor

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(Received April 21, 1933)

The Raman spectrum of water vapor at atmospheric pressure was obtained. Special precautions were taken to avoid parasitic light and a search made for the 1648 cm^{-1}, and 984 cm^{-1} shifts reported by Johnston and Walker. These shifts were not observed. A line was found which might be correlated with Mecke's $\nu(\sigma)$ but the evidence in this case is not conclusive.

INTRODUCTION

THE Raman spectrum of water vapor has been investigated by Daure and Kastler,[1] who found a single Raman shift 3654 cm^{-1}. Johnston and Walker[2] have observed three Raman shifts: 3654 cm^{-1}, 1648 cm^{-1}, and 984 cm^{-1}, which they correlate with Dennison's[3] ν_3, ν_2, and ν_1, respectively. R. Mecke[4] has pointed out that the 984 cm^{-1} shift cannot be correlated with $\nu(\sigma)$ but might be attributed to the vibration of the associated molecule H_2O-OH_2. The author has attempted to find the Raman frequency corresponding to Mecke's $\nu(\sigma)$, which should lie near $\nu(\pi)$.[4, 5]

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental arrangement used was similar to that used by Professor R. W. Wood[6] in his work with gaseous hydrogen chloride at atmospheric pressure. The scattering tube was of Pyrex, about 130 cm long and 50 mm in diameter. A plane Pyrex window was sealed on to one end of the tube. The other end was drawn out into a cone and bent at right angles to the axis of the larger tube. A 100 cc flask was sealed on to the conical end, and provision was made for evacuation. The diaphragm used was of brass and had an 8 mm aperture. Water was placed in the flask, and the water vapor pressure was maintained at one atmosphere by having the flask immersed in a bath of boiling water, since all the other parts of the tube were maintained at a temperature greater than 100°C by means of the mercury arcs and suitable heaters.

The light source used consisted of two double mercury electrode Pyrex mercury arcs about 80 cm long. The one had an internal diameter of 36 mm and carried a current of 9 amperes, while the other was 25 mm in diameter and carried a current of 4 amperes. The arcs and scattering tube were enclosed in a cylinder of highly polished sheet aluminum.

Before being used for making exposures, the scattering tube was thoroughly baked out and repeatedly evacuated in order to clear the tube from any gases which might cause contamination.

The image of the diaphragm was focussed on the slit of the spectrograph by means of an achromatic lens of about 35 cm focal length, placed at a distance of about two meters from the scattering tube. The spectrograph employed was the same as that described by the author[7] previously. Exposures were made by using one or two prisms and an F 4.5 camera lens, which gave a dispersion of 100 and 50 Angstroms/mm respectively at λ4200. The slit width used was between 0.06 and 0.07 mm but because of reduction of the size of the image when using the F 4.5 camera lens, the width of the lines on the photographic plate was less than 0.02 mm.

It can be seen by referring to Fig. 1, A, that two black lines run across the spectrum horizontally. These are caused by the light which is diffracted from the diaphragm. These black lines automatically furnish blanks of the incident

[1] Daure and Kastler, Comptes Rendus **192**, 1721 (1931).
[2] Johnston and Walker, Phys. Rev. **39**, 535 (1932).
[3] Dennison, Rev. Mod. Phys. **3**, 289 (1931).
[4] R. Mecke, Zeits. f. physik. Chemie **B16**, 407 (1932).
[5] R. Mecke, Phys. Zeits. **30**, 907 (1929).
[6] R. W. Wood, Phil. Mag. **7**, 744 (1929).
[7] D. H. Rank, J. Opt. Soc. Am. **23**, 84 (1933).

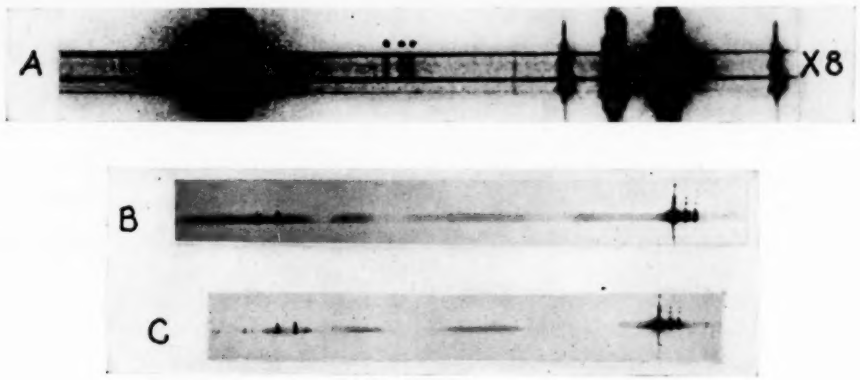

FIG. 1. A. The Raman spectrum of water vapor. B. The Raman spectrum of Pyrex glass. C. The spectrum of the mercury arc used.

radiation. Because of halation, faint Hg lines show up as dots on these black lines. Thus under the comparator, a Hg line looks much like a dumbbell while a Raman line does not have the knobs at both ends and is thus unmistakable. In order to furnish an additional blank of the incident radiation, a small finger mark was placed on the window just clear of the useful aperture. Sufficient light was reflected from this mark to give a complete blank spectrum. It can be seen by referring to the above figure that the Raman lines (3650 cm^{-1} excited by λ3650, λ3655, and λ3663), which are indicated by dots, are only in evidence between the two horizontal black lines; while Hg lines extend below the lower horizontal black line.

Using a single prism, the author was able to photograph the Raman lines $\Delta\tilde{\nu}=3650$ cm^{-1} excited by λ3650, λ3655, λ3663, and λ4047 with an exposure time of only two hours. With an exposure time of 47 hours, a line $\tilde{\nu}=21{,}950$ appeared which Johnston and Walker assign as a 984 cm^{-1} shift from λ4358. However, this line can be attributed within experimental error to a 3650 cm^{-1} shift from λ3906. This latter assignment seems most probable to the author, considering the great intensity of the 3650 cm^{-1} shifts and the increasing effectiveness of the shorter wave-lengths in exciting these long shifts. On these plates, taken with a single prism, the 3650 cm^{-1} shifts excited by λ3650 and λ3655 could be easily resolved.

Exposures were then taken with two prisms set for minimum deviation at λ4358. A 93-hour exposure showed all the lines which appeared on the plates taken with the single prism. In addition, on this plate a very weak line λ4238.6 appeared. This line might be assigned as a 3804 cm^{-1} shift from λ3650. However there is considerable doubt concerning this assignment, the increasing background preventing the observation of the two weaker lines excited by λ3655 and λ3663, which would definitely confirm this assignment. In order to test the very remote possibility of this line being due to double scattering from Pyrex, Mr. E. R. Bordner and the author have obtained the Raman spectrum of Pyrex. Use was made of a very fine bar of Pyrex which had been placed at our disposal through the courtesy of the Corning Glass Company. The filters used were the praseodymium filter, described by Wood and Collins,[8] and the sodium nitrite filter described by Pfund.[9] The excitation in this case is entirely by λ4358. Fig. 1, B, is an enlargement of one of the plates taken with Pyrex as the scatterer, while Fig. 1, C, shows the mercury as spectrum photographed through these filters. No lines were observed in the spectrum of Pyrex; only broad diffuse bands appear. The first of these bands has its center at 400 cm^{-1} and is about 150 cm^{-1} broad. The second has its center at 780 cm^{-1} and is about 50 cm^{-1} broad. These bands are only observable because they fall well within one of the praseodymium absorption bands. There seems to be a very heavy continuous Raman spectrum in the case of Pyrex in addition to the

[8] R. W. Wood and George Collins, Phys. Rev. **42**, 386 (1932).

[9] A. H. Pfund, Phys. Rev. **42**, 581 (1932).

band spectrum, as can be seen by referring to Fig. 1, B and C. It is absolutely certain that no Raman lines can be ascribed to double scattering from Pyrex in the light of these results.

The prisms were then set for minimum deviation at λ3900, and a 120-hour exposure was taken. None of the lines reported by Johnston and Walker[2] in this region were observed. It was found that faint Hg lines would interfere with the measurements of all the new lines reported by the above authors with the exception of the 984 cm^{-1} Stokes shift from λ4078 and the 984 cm^{-1} anti-Stokes shift from λ4078. The author was unable to find any evidence for the existence of these lines. No evidence was found for the Stokes shift from λ4047 which should fall midway between the pair of 3650 cm^{-1} Raman lines excited by λ3650 and λ3655 although this pair of Raman lines was easily resolved. No asymmetry of these lines could be noted. However all the Raman lines appeared to be about twice as broad as a sharp mercury line. Measurements of the plates give for the only Raman shift definitely observed 3650 $cm^{-1} \pm 3$ cm^{-1}.

Conclusion

The author was unable to find any evidence for the existence of the 984 cm^{-1} and 1648 cm^{-1} shifts reported by Johnston and Walker, although the intensity range used by the above authors appears to have been covered by a factor of two in the present investigation. One line which might be assigned as a 984 cm^{-1} shift from λ4358 can also be attributed to a 3650 cm^{-1} shift from λ3906 within experimental error. A line was found which, if excited by λ3650, might be correlated with Mecke's $\nu(\sigma)$. However because of the increasing background, the corresponding shifts from λ3655 and λ3663 could not be observed if they existed. Double scattering from Pyrex was definitely eliminated as the source of this line.

The Infrared Absorption Spectra of NO_2 and N_2O_4

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(Received April 17, 1933)

The infrared absorption spectrum of nitrogen peroxide has been investigated in the gaseous and liquid states, by using a prism spectrometer. Absorption bands were observed at 3.3μ, 3.89μ, 5.7μ, 6.14μ, 7.28μ, 7.85μ, 13.3μ and 15.6μ in the gaseous state, and at 3.65μ and 5.7μ in the liquid state. By heating the gas to a temperature of 150°C, it was found that the bands at 3.89μ, 5.7μ, 7.85μ and 13.3μ were due to N_2O_4, while those at 3.3μ, 6.14μ, 7.28μ and 15.6μ were due to NO_2.

THE infrared absorption of nitrogen peroxide has been investigated by Daniels,[1] and by Warburg and Leithauser[2] in the region 2μ to 7μ. They observed bands at approximately 3.4μ, 5.7μ and 6.12μ. von Bahr[3] observed bands at 6.1μ and 7.3μ for this substance.[4]

In order to obtain the fundamental frequencies and to attempt an analysis of the molecular structure of NO_2 and N_2O_4, it was decided to investigate the infrared absorption of nitrogen peroxide and extend the observations into the longer wave-length region.

Although a considerable amount of investigation on this equilibrium mixture has been carried out in the field of chemistry, very little is known at the present time concerning those properties which contribute to a knowledge of the structure of the molecules NO_2 and N_2O_4.

For an analysis of the structure of polyatomic molecules from the fundamental frequencies it is necessary to make certain assumptions regarding the binding forces between pairs of atoms. A mathematical treatment of the vibrational problem, even for the less complex polyatomic molecules, will in general give a set of equations which are less in number than the unknown quantities contained in them. These unknowns are the force constants and the angles describing the geometrical arrangement of the atomic centers. If the molecule contains a number of like atoms, and if there is good evidence of several equal bonds, the symmetry of the configuration will, in some cases, reduce the unknowns so as to render solutions of the equations possible.

Although the fundamental frequencies are in many cases obtained from the Raman spectra, it is necessary especially in the case of gases, to resort to the infrared absorption spectra for a more complete analysis.

APPARATUS

A Leiss prism spectrometer of the Wadsworth type was used. The experimental arrangement is shown in Fig. 1. N is a Nernst glower; M_1, M_2, M_3, M_4, concave mirrors; m_1, m_3, plane mirrors; m_2, Wadsworth mirror; S_1, S_2, slits; P, rocksalt prism; T, thermopile; G_1, primary galvanometer and thermo-relay amplifier; G_2, secondary galvanometer; K_2, scale for reading deflections of G_2; R, extension for rotating prism table; L, telescope for reading angle of rotation on scale K_1; S, shutter; C_1, C_2, absorption cells; W, mica or rocksalt window.

The spectrometer was enclosed in a felt-lined box. The cells, shutter and spectrometer were arranged so that they could be operated by one observer. A Moll thermo-relay amplifier, used in connection with a Zernike galvanometer for primary deflections and a sensitive Leeds and Northrup galvanometer for secondary deflections, proved to be very useful in studying the

* Laws Fellow in Physics.

[1] Daniels, J. Am. Chem. Soc. **47**, 2856 (1925).

[2] Warburg and Leithauser, Ann. d. Physik **28**, 313 (1909).

[3] Eva von Bahr, Ann. d. Physik **33**, 585 (1910).

[4] During the course of this investigation C. R. Bailey and A. B. D. Cassie have reported observations on this gas to 18μ and report several additional bands; Nature **131**, 239 (1933).

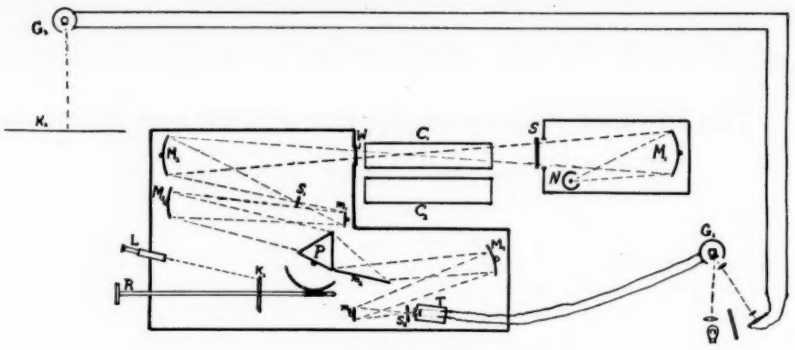

FIG. 1. Experimental arrangement.

longer wave-length regions where the emission of the glower was comparatively weak. A Moll linear thermopile, enclosed in an air-tight brass case and placed immediately behind the exit slit, was used to detect the radiation.

The spectrometer was adjusted according to the method suggested to the author by W. W. Sleator of the University of Michigan. The prism was first adjusted so that the entering beam of light striking the face of the prism is reflected back through the entrance slit so that the reflected image exactly fills the slit. The angle of incidence of the mercury green line (5461) was then computed from the minimum deviation formula and the known index of refraction of NaCl at this wave-length. The prism was then turned through this angle and the Wadsworth mirror adjusted so that the Hg green line filled the opening of the second slit. The spectrometer was then checked with the Hg emission line at 1.014μ and the CO_2 absorption band at 4.26μ. The indices of refraction for NaCl, taken from tables,[5] were plotted on a graph with wave-lengths through a range 0.5μ to 16μ. On a separate graph the angle of minimum deviation was plotted with the indices of refraction. The wave-length for any angle of the prism table could then be determined by referring to the two graphs and correcting for the change in the indices of refraction due to the temperature of the prism.

The sensitivity of the receiving apparatus was sufficient to obtain readings as far as 16μ with the NaCl prism, although the transmission of rocksalt in this region is small.

[5] Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 47.

PREPARATION OF THE GAS

Pure nitrogen peroxide was obtained by heating C. P. copper nitrate and condensing the gas by cooling with a mixture of ice and CaCl. The apparatus, shown in Fig. 2, was made

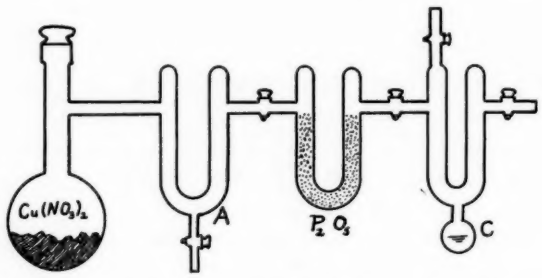

FIG. 2. Apparatus for preparing nitrogen peroxide.

entirely of Pyrex glass. In chamber *A*, water present in the copper nitrate was condensed, the gas passing through a drier of P_2O_5 and being condensed at *C*. The gas was forced into the absorption cell by partially evacuating the cell. In this process it was again passed through P_2O_5 to insure dryness.

ABSORPTION SPECTRA OF NO_2 AND N_2O_4

The spectrum of nitrogen peroxide was mapped from 2μ to 16μ, by using absorption cells 10 cm in length with rocksalt windows and slit widths ranging from 0.08 mm to 0.5 mm. Strong absorption bands were observed at 3.3μ, 5.7μ, 6.14μ, 7.28μ, 7.85μ, 13.3μ and 15.6μ, and a weak band at 3.89μ. These bands with their approximate intensities are shown in Fig. 3.

The observations on these bands were taken at a pressure of one atmosphere. The low

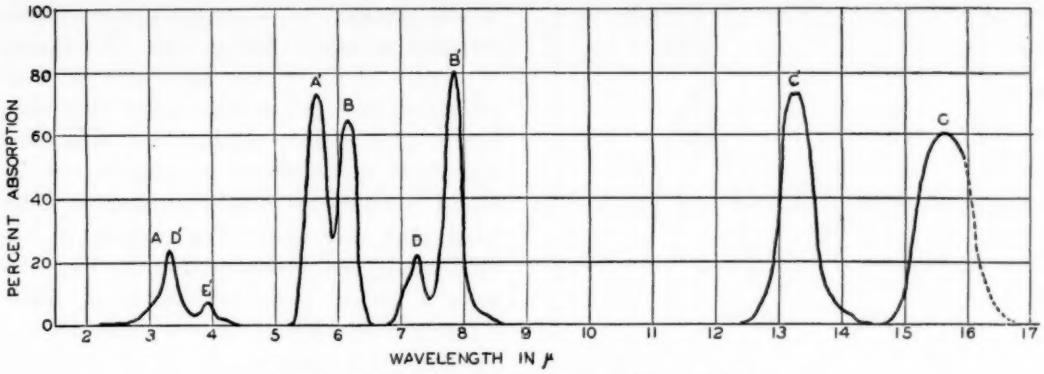

FIG. 3. Infrared absorption spectra of NO_2 and N_2O_4.

intensity of the band at 3.89μ did not permit accurate measurement of its wave-length.

It is known from chemistry that at ordinary temperatures this gas is a mixture of NO_2 and N_2O_4. At about 150°C, however, the gas consists entirely of NO_2.

In order to determine which bands were due to NO_2 and which were due to N_2O_4, an investigation of the infrared absorption of this gas was undertaken at different temperatures. The gas was heated by using an absorption cell with nichrome wire wound about its outer surface and insulated from the surface with asbestos. The temperature was regulated by the amount of current passed through the nichrome coil, and observed by inserting a thermometer in a side tube attached to the absorption cell.

For the region, 2μ to 8μ, mica windows were used with cells 35 cm in length. The results for this region are shown in Figs. 4 and 5. The bands at 3.89μ, 5.7μ and 7.85μ are due to N_2O_4, since they decrease in intensity and finally disappear at the higher temperatures and increase in intensity at the lower temperatures. The bands at 6.14μ and 7.28μ increase in intensity as the temperature is raised and decrease when the temperature is lowered, and are therefore attributed to NO_2. The band at 3.3μ exhibits a peculiarity inasmuch as it decreases slightly with increase in temperature and increases in intensity with decrease in temperature, but does not disappear at the higher temperatures as we would expect if it were due only to N_2O_4. This suggests that the 3.3μ band may be a characteristic frequency of both NO_2 and N_2O_4, and that the absorption bands of both gases in this region are nearly superimposed.

For the region, 8μ to 16μ, it was necessary to use rocksalt windows on the absorption cells. To avoid breaking of the rocksalt windows, the cells were first fitted with mica windows. Openings were then cut in the mica and the rocksalt windows mounted over these openings

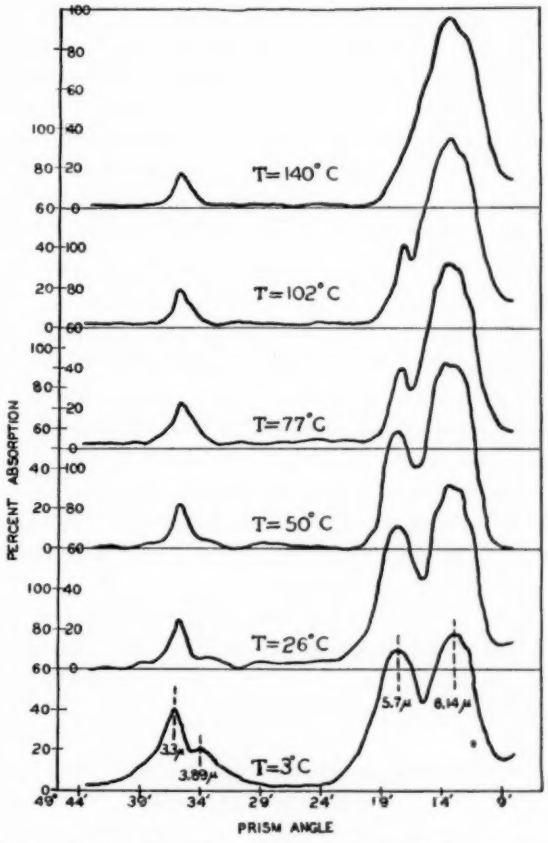

FIG. 4. Infrared absorption of nitrogen peroxide at different temperatures in the region 2μ to 7μ.

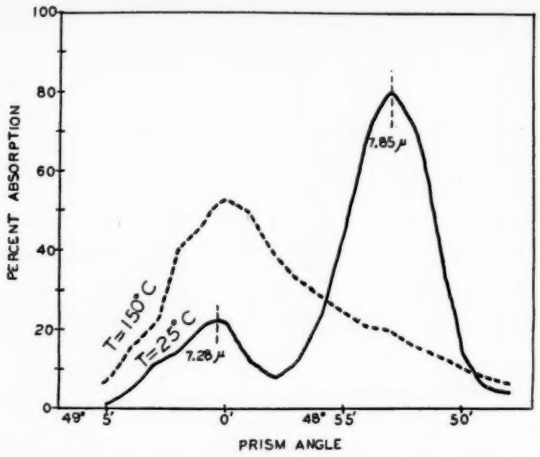

FIG. 5. Infrared absorption of nitrogen peroxide at different temperatures in the region 7μ to 8μ.

with Duco cement. This reduced the strain on the rocksalt and prevented cracking when the cell was heated.

Observations in this region were taken at temperatures of 25°C and 150°C. The band at 13.3μ disappeared entirely at 150°C while the 15.6μ band remained at about the same intensty.

These experiments were sufficient to determine with some degree of certainty which bands could be attributed to the two different types of molecules present in this gas mixture. The bands designated as A, B, C and D in Fig. 3 are due to NO_2 while the bands A', B', C', E', and possibly a band near $3.3\mu(D')$ are due to N_2O_4.

It may be remarked here that Bailey and Cassie[4] report the disappearance of all the bands except bands B and C at a temperature of 100°C, and apparently did not observe the band at 7.28μ. The author has examined the 3.3μ and 7.28μ bands at temperatures as high as 240°C with some care. Both bands remained at these high temperatures, the 7.28μ band increasing considerably in intensity.

The low transmissibility of NaCl in the region of 16μ did not permit complete observation of the band, C. Bailey and Cassie give the wavelength of this band as 15.6μ.

INFRARED ABSORPTION OF LIQUID NITROGEN PEROXIDE

In order to determine whether or not the 3.3μ band was common to both NO_2 and N_2O_4, it was decided to investigate the infrared absorption of liquid N_2O_4. Since this liquid boils at about 21°C, it was necessary to construct an absorption cell which could be cooled well below this temperature. The difficulties encountered in obtaining a suitable cell for this liquid were many, and a number of cells were tried and discarded. The details of the cell finally used are shown in Fig. 6. Two sheets of mica 7 inches long, 1.5 inches in width and 0.1 mm in thickness were separated by a mica "gasket" 0.1 mm in thickness and clamped between two slotted brass strips. The top was left open so that a small pointed tube could be inserted between the mica plates. The upper portion of the cell was surrounded by a cooling chamber. The cell was filled with liquid N_2O_4 by forcing gaseous nitrogen peroxide into the cell through the small pointed tube inserted at the top, and condensed by cooling. After the cell had been filled the top was closed by clamping the mica sheets together with the brass insert B, and sealed over with soft wax. The cell was then placed in the light path so that the beam passed through the lower portion. An empty cell of the same thickness of mica was attached so that both cells could be thrown alternately in and out of the path of light.

The results were not very gratifying and were made less certain due to the condensation of water vapor on the windows of the absorption cell. However, in addition to the H_2O bands at

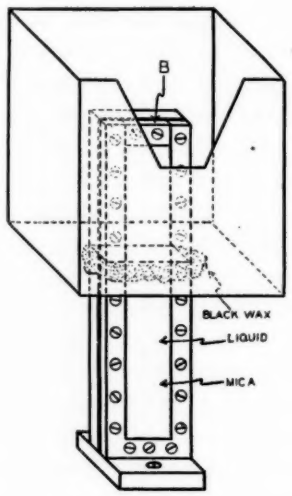

FIG. 6. Cell used in studying liquid N_2O_4.

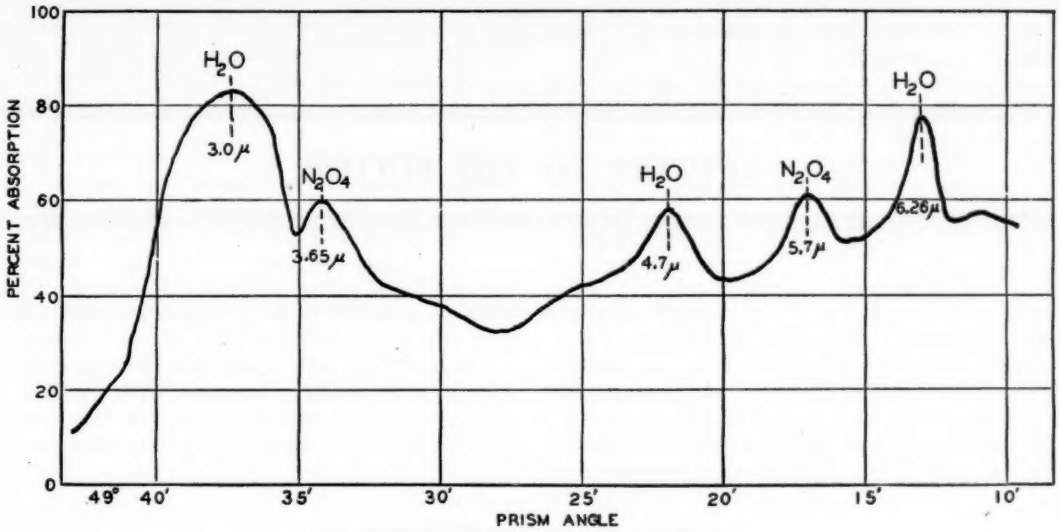

FIG. 7. Infrared absorption of liquid N_2O_4.

3μ, 4.7μ and 6.26μ, bands due to N_2O_4 were observed at 3.65μ and 5.7μ, as shown in Fig. 7. The nearness of the broad H_2O band at 3μ made the wave-length measurements of the 3.65μ band uncertain, and it is probable that its true wave-length is somewhat less than this value.

DISCUSSION OF BANDS

These results show that N_2O_4, at least in the liquid state does have an absorption band in the region of the 3.3μ band of NO_2. The fact that the peak of the 3.3μ band shows no appreciable shift at the higher temperatures suggests that the N_2O_4 band in this region has approximately the same frequency as the NO_2 band in the gaseous state. It is interesting also to note that this summation frequency, $\nu_1+\nu_3$, for N_2O_4 has almost the same value as the frequency, $\nu_1+\nu_3$, for NO_2 as shown in Table I. The observed value for this frequency is 3008 cm^{-1}.

The frequencies and wave-lengths of the absorption bands for NO_2 and N_2O_4 are shown in Table I. ν_1, ν_2, and ν_3 are assigned as the fundamental frequencies. The assignment in N_2O_4 is only tentative. It is probable that this molecule has more than three distinct fundamental frequencies. However, only three strong bands appear in the infrared absorption of this substance. The apparent simplicity of this spectrum makes it appear probable that the N_2O_4 molecule is symmetrical in structure.

TABLE I.

Band	Observed frequency in cm^{-1}	Calculated frequency in cm^{-1}	Combination	Wave-length in μ
NO_2				
A	3008	3001	$\nu_1+\nu_3$	3.30
B	1628		ν_3	6.14
C	641		ν_2	15.60
D	1373		ν_1	7.28
N_2O_4				
A′	1754		ν_3	5.70
B′	1274		ν_1	7.85
C′	752		ν_2	13.30
D′	3008	3028	$\nu_1+\nu_3$	3.30
		2500	$\nu_2+\nu_3$	
E′	2570	or	or	3.89
		2526	$2\nu_1$	

The author wishes to express his thanks to his advisor, Dr. L. T. More, and to other members of the staff of the Physics Department for suggestions and help during the course of this investigation.

LETTERS TO THE EDITOR

In response to requests from our contributors, and after a canvass of the opinions of the Editorial Board, the Journal of Chemical Physics wishes to announce that a "Letters to the Editor" section will be carried by the Journal. This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual page charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Raman Spectra of the Dichlorobenzenes

In connection with a study of the Raman spectra of benzene derivatives, the earlier work on the three isomeric dichlorobenzenes has been repeated.[1, 2, 3] The results reported at this time were obtained with the technique described elsewhere by one of us and Donald H. Andrews.[4] The following Raman frequencies were found:

Ortho-dichlorobenzene:—154 (10), 203 (3), 239 (1b), 330 (0b), 430 (1), 469 (1), 483 (2), 658 (5), 756 (0b), 860* (1b), 1020 (1), 1041 (10), 1129 (5), 1160 (1b), (1228) (0), 1274 (1b), 1577 (4), 1607 (0b), 2994* (1), 3073 (10), 3146 (3).

Meta-dichlorobenzene:—178 (3), 202 (3), 216 (2), 366 (1), 399 (4b), 428 (2), 530* (0), 666 (4), 999 (10), 1018* (0), 1070 (3b), 1109* (2), 1126 (4), 1240 (0), 1425* (0), 1456* (0), 1544* (0), 1579 (5b), 1625* (0), 3076 (10), 3152* (2).

Para-dichlorobenzene:—302 (4), 333 (8), 355* (1), 627 (5), 710* (00), 748 (10b), 885* (0), 942* (0), 1070 (3), 1087 (2), 1109 (10), (1147) (0), 1170* (1), 1217* (0), 1294* (0), 1331* (0), 1379 (0), 1576 (8), 1630* (1), 2953* (0), 3079 (10), 3153* (2), (3213)* (0).

The numbers in parentheses after the frequencies are visual estimates of intensity. The frequencies in parentheses are so weak as to be doubtful. The lines were excited by the blue and violet mercury lines separately by using filters.

The line reported by Mlodzianowska at 625 in the ortho compound was not found. The lines which he found at 21,565 cm^{-1} appear with violet excitation and not with blue and hence should be assigned to 3143 rather than 1376. Filters were not used in his work and hence this point could not be decided as the plate is rather insensitive in the region of the 3143 line excited by the blue mercury line. The lines marked with an asterisk are reported here for the first time.

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Chemistry Laboratory,
The Johns Hopkins University,
June 15, 1933.

[1] Dadieu and Kohlrausch, Monats. f. Chem. **52**, 379 (1929).

[2] Mlodzianowska, Zeits. f. Physik **65**, 124 (1930).

[3] Dadieu, Kohlrausch and Pongratz, Monats. f. Chem. **61**, 426 (1932).

[4] Murray and Andrews, J. Chem. Phys. **1**, 406 (1933).

A Name and Symbol for H^{2}*

Various lines of evidence lead to the conclusion that the isotope of hydrogen of atomic weight two has properties which differ considerably from those of the isotope of hydrogen of mass one. Thus, the boiling points of the liquid hydrogen are appreciably different;[1] the two isotopes are rapidly separated in electrolysis;[2] the equilibrium constants involving the two atoms of hydrogen have been shown to be appreciably different;[3] it is found that the melting points and the boiling points of water containing the two varieties of isotopes are not the same;[4] and finally, the refractive index of water varies with the amount of the heavier isotope present.[4, 5] It appears very probable that similar differences will be found in other compounds, depending upon whether the one or the other isotope is

* Publication approved by the Director, Bureau of Standards, Department of Commerce.

[1] Urey, Brickwedde and Murphy, Phys. Rev. **40**, 1 (1932).

[2] Washburn and Urey, Proc. Nat. Acad. Sci. **18**, 496 (1932).

[3] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

[4] Washburn, Smith and Frandsen, J. Chem. Phys. **1**, 288 (1933); Washburn and Smith, J. Chem. Phys. **1**, 426 (1933).

[5] Lewis. J. Am. Chem. Soc. **55**, 1297 (1933). J. Chem. Phys. **1**, 341 (1933).

present in them. Moreover, the electrolytic method for the separation of the isotopes has proved to be very effective in the separation,[5] and it thus seems certain that very appreciable amounts of the heavy isotope will be available for experimental work.

It is inconvenient to refer to the heavy isotope of hydrogen as "hydrogen two" because this is so easily confused with the usual methods of referring to chemical compounds. This difficulty is not met in the case of any other isotopes because of the large mass numbers, and thus leads to no confusion, but in the case of hydrogen it seems desirable that special names should be given to the isotopes of hydrogen.

Two procedures might be followed in regard to this. In the first place, we might reserve the name hydrogen for the H^1 isotope and give a new name to the H^2 isotope or, second, we might reserve the name hydrogen for the natural mixture of the hydrogen isotopes, or for any other mixture where the isotopic composition is not important, and then give special names to both the H^1 and H^2 isotopes. After considerable thought, we believe that this latter procedure is the better one. We wish to propose that the names for the H^1 and H^2 isotopes be protium and deuterium, respectively, from the Greek words protos and deuteros, meaning first and second. These names will permit the formation of the usual prefixes and suffixes in common use in chemistry. Thus, we will have protides and deuterides, protoxyl and deuteroxyl, protates and deuterates, proto-compounds and deutero-compounds, in analogy to hydrides, hydroxyl, hydrates, hydro-compounds, etc.

If the H^3 isotope is discovered, we would recommend to the discoverer the consideration of the name tritium for it.

Lewis (private communication) proposed the name deuton for the deuterium nucleus. We do not wish to propose any name for this nucleus, other than the deuterium nucleus, or if it is convenient to so refer to it, the hydrogen two nucleus, because it is not a fundamental particle and we hesitate to suggest a name which would classify it along with the proton, neutron, electron, photon, as fundamental particles. However, in case workers in the field of nuclear transmutations find such a term desirable, it would appear to us that the name deuteron would follow the Greek derivation better.

The symbols of protium and deuterium should be, we believe, H^1 and H^2 to be read protium and deuterium, respectively. These symbols show that these two isotopes are indeed hydrogen and these symbols are in accordance with the usual symbols for other isotopes. It is perhaps somewhat confusing at first to read these symbols as protium and deuterium, but certainly it is no more so than in many other cases in common use.

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